Subsurface Phosphorus Transport through a no-till Field in the Semiarid Palouse Region

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AUTHORIZATION TO SUBMIT THESIS

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ABSTRACT

Heavy application of fertilizers containing nitrogen and phosphorus to soils causes surface water quality degradation because the nutrients flow out of the agronomic systems and enter water bodies in large quantities, causing algal blooms and eutrophication. Extensive studies focusing on phosphorus as a surface water pollutant from agronomic systems have been conducted in the many regions of the United States, however, there has been a lack of studies completed in the semiarid Palouse region of eastern Washington and western Idaho. The goal of this research was to better understand how no-till farm management has temporally altered soil P availability for off-site transport through an artificially drained catchment at the Cook Agronomy Farm in Pullman, WA. Preferential flow pathways were also characterized in extracted cores. Dissolved reactive P (DRP) concentrations in subsurface drainage from an artificial drain exceeded TMDL threshold concentrations during numerous seasonal high flow events over the two-year study time frame. Soil analyses of samples collected in 1998, 2008, and 2015 show a highly variable distribution of water-extractable P across the sub-catchment area, and translocation of P species deeper into the soil profile since implementing no-till practices. We hypothesized that a greater network of macropores from lack of soil disturbance allow for preferential flow of water rich in dissolved nutrients deeper into the subsurface and to the artificial drain system. Simulated flow experiments on soil cores from the study site showed large-scale macropore development, extreme variability in soil conductivity, and high P adsorption potential for the soils, suggesting a disconnect between P movement through macropore soil and subsurface drainage water rich in DRP at the artificial drain line outlet.

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DEDICATION

This Master's in Water Resources thesis is dedicated to my friends and family who gave me overwhelming support and much needed mental stability during my time at the University of Idaho. Especially my parents, Robin and Kevin, my fellow graduate students (Max Ross, Shane Stoner, Danika and Ryan Hill-Paulus, and Dillon Shults), and the other amazing people that contributed to this unforgettable experience.

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CHAPTER ONE: SOIL AND WATER PHOSPHORUS DYNAMICS AT THE COOK AGRONOMY FARM

INTRODUCTION

Phosphorus Loading: A Complex Issue

Phosphorus (P) is an essential element for plant growth and is commonly applied as an inorganic fertilizer. However, excess P can be detrimental to water quality when it leaves agronomic systems because it causes harmful algae growth (Carpenter et al., 1998; Downing, 2013; Schindler, 1974, 1977, 2012; Schindler and Vallentyne, 2008). Phosphorus typically binds tightly to soil particles and does not move below the rooting zone. Because of this, most management plans focus on reducing particulate P by targeting surface runoff and point source P pollution, which was initially shown to be successful. However, after decades of best management practice implementation, P in surface waters continues to be an issue in many areas of the country, and the largest contributor to water quality degradation is now believed to be non-point sources (Jarvie et al., 2013; Kleinman et al., 2011). It is proposed that "legacy P" in soils and sediments are a major source of the continued P loading in surface waters (Muenich et al., 2016; Powers et al., 2016; Kleinman et al., 2011; Jarvie et al., 2013; Søndergaard et al., 2003).

Total phosphorus in water samples is comprised of particulate and dissolved species. Dissolved P, often referred to as dissolved reactive P (DRP), is the form that directly decreases water quality because it is available for plant uptake (Kleinman et al., 2002; Turner et al., 2004). However, particulate P also poses risks for surface water quality degradation because P can be desorbed or solubilized to replenish or increase dissolved P concentrations (Turner et al., 2002; Liu et al., 2014), thereby releasing P to the solution phase and contributing to environmentally-available P. The potential of particulate P to contribute to the dissolved P load is dependent on its species, with some species more readily available than others to partition into the soluble P phase (Shigaki and Sharpley, 2011). In freshwater ecosystems, typically the percentage of P in organic biota or adsorbed onto particulates is greater than 90% of total P, with the 10% fraction as the more biologically available DRP (IDEQ, 2007). In impaired systems, a larger proportion of the total P is in the soluble DRP form that is directly available for plant uptake and can pose water quality problems if conditions allow algae growth (IDEQ, 2007).

Dissolved P in runoff has been identified as a primary nutrient of concern for water quality. This is especially true for agriculture systems, where over-application of fertilizer has led to many soils becoming enriched in P (Kleinman et al., 2011). Since soils that are enriched in P have a greater potential to supply dissolved P to runoff (Vadas et al., 2005), agricultural soils can be sources of P rather than sinks. A prominent example of excess nutrient accumulation is occurring in Lake Erie, which was considered a BMP success in the 1980's and 1990's that led to dramatic water quality improvements; however, Lake Erie is currently experiencing a phase of re-eutrophication, most noticeably in the shallowest region of the Western Lake Erie Basin (WLEB) (Ho and Michalak, 2017; Jarvie et al., 2017). Nuisance algal blooms are becoming more frequent, and in 2014, water quality issues cut off drinking water supply to 400,000 people in the WLEB (Smith et al., 2015c). Current issues have been directly linked to higher DRP loads, which have been steadily increasing since the early 2000's. It is proposed that the increase is a consequence of reduced tillage compounded with higher seasonal flows due to climate change (Jarvie et al., 2017). Jarvie et al. (2017) argues that no-till management, while reducing surface runoff and particulate P loads, is increasing the hydraulic connectivity of dissolved P into the watershed. In fact, research has shown that even though no-till is successful in reducing total P lost from a system, it can increase dissolved P loading (Shipitalo et al., 2013; Smith et al., 2015b) by as much as double in some cases (Smith et al., 2015a). The proposed mechanism of this increase is that reduced tillage leads to preservation of subsurface preferential flow pathways that are able to transmit water rich in dissolved P varieties to artificial drainage systems that directly influence nearby surface water bodies. Furthermore, broadcasting of fertilizer with little to no soil incorporation, can create nutrient stratification and can further exacerbate this issue (Kleinman et al., 2003).

Preferential Flow Pathways and Artificial Drains

Recent studies suggest that subsurface transport of P may be a larger contributor to off-site P loading than suggested by conventional knowledge (King et al., 2014; Smith et al., 2015a, 2015b; Kleinman et al., 2015a). These studies propose that P moves in the subsurface through an interconnected network of macropores or soil cracks, creating preferential flow pathways that allow water rich in nutrients to bypass the soil matrix and rapidly enter the waterways through artificial drains. Clay and silt rich soils are especially vulnerable to macropore structure (Kleinman et al., 2015a). Kleinman et al. (2015a) discovered heavy concentrations of DRP and particulate P in the leachate through the soil of silty loams and soils with higher clay content. Djodjic et al. (2004) also found that finer textured soils were more likely to transmit P through the soil and into the leachate because of a higher degree of structural integrity that helps preserve macropores. Macropores (defined as a pore size greater than 75 µm (Bouma, 1991)) can be cracks or fissures in the soil, natural soil pipes, decayed root channels, pores or voids formed by animal fauna such as earthworms (Beven and Germann, 1982). These preferential flow pathways are more likely to stay intact under conservation and no-till practices with a lack of soil disturbance.

Artificial drainage systems are a widely implemented agricultural practice used across the United States, especially in the Midwest, where fields would be unproductive without a mechanism to drain excess moisture from the soil (Keller et al., 2008; Kleinman et al., 2015b; Shober et al., 2017). Artificial drains, or artificial drainage systems, have been used for decades to lengthen the farming season, and they are commonly used in the Palouse region of western Idaho and eastern Washington to increase crop productivity in the lower topographic locations where restricted infiltration causes ponding on the surface (Keller et al., 2008). Water quality issues can arise when these artificial drainages in an agronomic system are draining runoff that is rich in nutrients directly into nearby waterways and thus entering the watershed. Preferential flow pathways such as macropores with high hydraulic conductivity further increase the ease at which P and other agrochemicals are transported to nearby water bodies. Smith et al. (2015a) measured artificial drainage in the St. Joseph River watershed in northeast Indiana. They found that artificial drain discharge peaks occurred simultaneously, or in some cases, before the surface runoff peaks. According to Smith et al. (2015b), this contradicts conventional wisdom that artificial drain waters result from water released from the soil matrix, which was supported by recent research from Evaristo et al. (2015) that concludes that plants draw from a separate soil water reservoir than the groundwater recharge or streamflow. Evaristo et al. (2015) further suggest that the water that supplies streams and groundwater moves through the subsurface seemingly unmixed with the water available for plant uptake, which may have significant impacts on nutrient flow and plant uptake dynamics.

Conventionally, it is thought that surface runoff peaks should precede artificial drainage peaks because full infiltration of precipitation water through the subsurface should take longer than initial overland runoff. “Simultaneous peak discharge in tile and surface runoff indicates connectivity of surface water to the tile, most likely through macropore flow (Smith et al., p. 499, 2015b).” Smith et al. (2015b) proposed that macropores provide a direct route of transfer for water rich in dissolved nutrients to bypass the soil matrix, where P could become potentially sequestered or taken up by plants. From their research sites, they found that 49% of soluble P and 48% of total P left with the artificial drainage water. This research was further supported by Frey et al. (2016), who found that macropores in their clay loam soil contributed to more than 98% of the artificial drain discharge and solute load. These findings demonstrate that ignoring artificial drains as a source for P loading into the environment could result in a major underestimation.

Regional Overview

The topography of the dryland cropping region of the Palouse in western Idaho and eastern Washington consists of rolling hills with varying aspects and slopes, leading to differences in irradiance, soil water content, and soil temperature. Excessive tillage on the steep topography over the last 100 years resulted in high soil erosion and translocation of topsoil throughout the Northwest Wheat and Range Region (NWRR) (Brooks et al. 2012; Montgomery et al. 1999; USDA, 1978; Kaiser, 1961). In 1978, it was estimated that all the original topsoil had been lost from 10% of the cropland, and one-fourth to three-fourths of the original topsoil has been lost from 60% of the cultivated area in the Palouse basin (USDA, 1978). As a result, the extreme variability in topography and soils, crop yields and nutrient uptake can vary greatly within a single managed field (Huggins et al., 2010; Fiez et al., 1994, 1995).

High erosion rates from decades of conventional tillage practices in the Palouse region have led to a shift towards conservation tillage by many farmers. The conservation tillage practices include mulch or no-till techniques. This shift has drastically reduced the amount of topsoil loss around the Palouse, but provides a prime environment for the preservation of preferential flow pathways, especially in the fine textured soils of this area. As previously discussed, conservation tillage can be successful in reducing P loading by minimizing particulate P bound species in surface runoff, but can also lead to significant increases in the dissolved P load through the subsurface (Smith et al., 2015a).

In 2013, a drain gauge lysimeter (Drain Gauge G3 Passive Capillary Lysimeter (Decagon Devices (Pullman, WA)) was installed at the Cook Agronomy Farm located on in the Palouse region in Pullman, WA. The field in-situ drain gauge lysimeter collects subsurface flow that can be pumped for collection through an intact soil core (two feet long and 10 inches in diameter). During installation, an extensive macropore network was discovered (Figure 1.1) at a depth of five feet below the surface that has been shown to receive the majority of flow by preferential pathways with an immediate hydraulic response during simulated rainfall events (Payne et al., 2012).

FIGURE 1.1. A soil core taken from the Cook Agronomy Farm (CAF) from Dr. Erin Brooks and his team in 2013 at a depth of approx. five feet showing macropore and preferential pathway development.

According to the Web Soil Survey (NRCS, 2017), the saturated hydraulic conductivity (K_s) of soils within the Cook Agronomy Farm range from 0.4 m/day (Naff silt loam) to 0.8 m/day (Palouse silt loam), with nearby Latah County (ID) reporting a similar 0.8 m/day (Barker, 1981). However, Brooks et al. (2012) found large lateral K_s variability from a hillslope plot located within the region, with values decreasing rapidly from 101 m/day to 6 m/day in the first 0.1 m, and an exponential decline thereafter. They attributed this large surface layer variability to macropore structure. We hypothesize that in a long term, no-till managed farm system (i.e., the Cook Agronomy Farm) macropores are extensively established, and are a major conduit for subsurface flow and resulting in artificial drainage water rich in dissolved phosphorus.

A common natural water quality benchmark across the United States for total P is 0.10 ppm (or mg/L), which was proposed in 1986 with the Environmental Protection Agency (EPA) Gold Book. A more conservative number of 0.030 ppm was proposed in 2000 for the Columbia Plateau sub-ecoregion streams (IDEQ, 2007). Our study site, the Cook Agronomy Farm, is located in the Palouse Hills within the larger Columbia Plateau ecoregion of Washington, western Idaho, and northern Oregon (USEPA, 2013). Even though the site for this study is technically contained in an area of Washington, with no phosphorus total maximum daily load (TMDL) for the local watershed, less than three miles to the east, across the Idaho border, a local TMDL of 0.10 ppm TP was established for the Palouse River Subbasin in 2005 and the Palouse River Subbasin (South Fork) in 2007. These TMDLs are a higher threshold than the previously suggested nutrient criterion standard for the Columbia Plateau because they are deemed agricultural watersheds (IDEQ, 2005, 2007). The main CAF artificial drain empties into Missouri Flat Creek (Figure 1.2), which is also supplied by several other agriculturally influenced ditches and artificial drainage systems before eventually draining into the South Fork Palouse River in Pullman, WA.

FIGURE 1.2. Map showing water sample locations at the CAF. Red circles are locations where an automatic ISCO sampler is located. The green circle is an in-situ drain gauge lysimeter and the yellow circle refers to where the phosphate sensor was deployed along Missouri Flat Creek during the spring of 2016 (see "*Water Collection and Analysis*").

Current Research Gaps

With the increasing availability of GPS tracking and guidance systems, and crop yield monitors and variable rate fertilizer application technologies, precision agriculture techniques are more readily being implemented by farmers. This typically results in fields being divided into multiple management zones and treated with variable fertilizer rates (Flemming and Westfall, 2000). To date, the focus in precision agriculture has been on varying nitrogen rates. In the NWRR, nutrient management also includes annual addition of P fertilizer. Phosphorus fertilizer application rates are based on historical application rates (Koenig, 2007). Given the variability in soil properties, and current efforts to increase precision agriculture management, there is a need to develop site- and crop-specific P fertilizer application strategies by studying the distribution of available P in soils to increase fertilizer efficiency and minimize off-site transport.

Despite the annual application of phosphorus fertilizer at the Cook Agronomy Farm (CAF) in Pullman, WA, there are few data exploring the net phosphorus exchange within the site. Previous research by Rich Koenig (2007) showed there was a large spatial variability between acetate-extractable P concentrations in the soil across the CAF. The 185 samples collected from the first four inches of soil, ignoring P concentrations in the subsoil. Considering that artificial drainage is supplied by subsurface flow, data are required for a larger range of the soil profile. Recent studies at the CAF have focused on understanding preferential flow hydrology in regards to nitrate concentrations (Kelley et al., 2015; Keller et al., 2008) and dissolved organic matter (DOM) (Bellmore et al., 2015) leaving the artificial drain. However, limited research has been done in the Palouse region to determine P concentrations in runoff from agronomic systems. Research shows initial high nitrate concentrations in discharge with the start of artificial drain flow, depending on the highly seasonal precipitation (See “*Site Background and Description*”). Concentrations of nitrate in drainage water decrease as the growing season commences with higher peak nitrate flow corresponding to high precipitation events, which are thought to rapidly mobilize soil water rich in nitrate and other dissolved constituents to the artificial drain (Keller et al., 2008; Kelley et al., 2017). High precipitation events have also been shown to rapidly transport dissolved organic matter to the artificial drain (Bellmore et al., 2015). Monitoring of P concentrations from the artificial drainage at CAF is needed to determine the P dynamics and loading potential from agronomic systems in the Palouse region and to manage local water quality standards. To reduce off-site transport of P, understanding the mechanisms for P transport and information on best management practices for the various soil types is required.

One of the greatest challenges for improving agricultural productivity and environmental sustainability is accurate prediction of the amount of P that will be transported to surface waters. The P loading problems to surface waters occur because nutrient management plans do not correctly account for P loading potential of soils and availability of P for offsite transport. The core of the problem is that the soil tests were designed to monitor P availability for plant nutrient management. Currently, several methods to test soil P are available, including the Mehlich-3 test (1984), the Olsen P test (1954), and the Bray & Kurtz method (1945). However, it has been suggested that these methods of P extraction from soils incorrectly determine available P for runoff because the extractants, either acidic or alkaline, mobilize P that is not readily transported in runoff or flow through water (Davis et al., 2009). To accurately assess watershed health, a soil test to determine the P loading potential of agriculturally managed soils is needed. Kovar and Pierzensky (2009) proposed that water-extractable P (WEP) is a good method to determine the amount of P available for runoff or leaching. Kleinman et al. (2002) and Pote et al. (1996) determined that there was a strong correlation between the water-extractable soil P and dissolved reactive P concentrations in runoff. After recognizing that subsurface P loss can be a major contributor to the P load in agricultural watersheds (Williams et al., 2016; King et al., 2015; Kleinman et al., 2015a), Shober et al. (2017) found that incorporating soil WEP into current predictive models improved predictions for dissolved P loads in artificially drained systems. Paired with drainage water analysis, measuring the WEP of CAF soils at various topographic locations, depths, and years will provide vital information on the P loading potential in the CAF watershed.

Research Goals

The goal of this research study is to better understand phosphorus availability for off-site transport in a catchment at the Cook Agronomy Farm and to determine the processes responsible for surface and subsurface flow of phosphorus. To achieve this goal, three project objectives were completed:

Objective 1. Characterize phosphorus availability as a function of depth, time (1999-2015), and spatial variability throughout a drainage catchment at the CAF since the implementation of no-till farm management.

To accomplish objective one, we analyzed P leaching potential of the soils by the WEP method for archived soil samples from 1999, 2008, and 2015 at nine geo-referenced points (three at toe slope, three mid-slope, and three top-slope locations) and at three depths (0-10 cm, 20-30 cm, and a deep subsurface sample at ~100 cm).

Objective 2. To better understand how preferential flow pathways contribute to phosphorus movement through the soil profile and determine the conditions when macropores become "activated" and allow for subsurface flow.

To accomplish objective two, soil cores harvested from three locations at CAF to represent varying slope positions (toe slope, mid-slope, top slope) were subjected to simulated precipitation events as well as ponding conditions. Core leachate was analyzed for DRP during high- and low-intensity rainfall events. A ponded water experiment with a spiked solution of P and EC provided information on P movement through the intact soil cores. Dye solution was applied followed by excavation and image analysis to interpret flow pathways. Soil samples taken during core harvesting were analyzed for soil P availability as a function of depth.

Objective 3. Understand surface and subsurface flow that result in phosphorus loading into a nearby stream (Missouri Flat Creek) as a function of time and seasonal variability by comparing P species within the artificial drainage and surface runoff from CAF to Missouri Flat Creek, a stream system that receives its main source of flow from agricultural runoff (Figure 1.3).

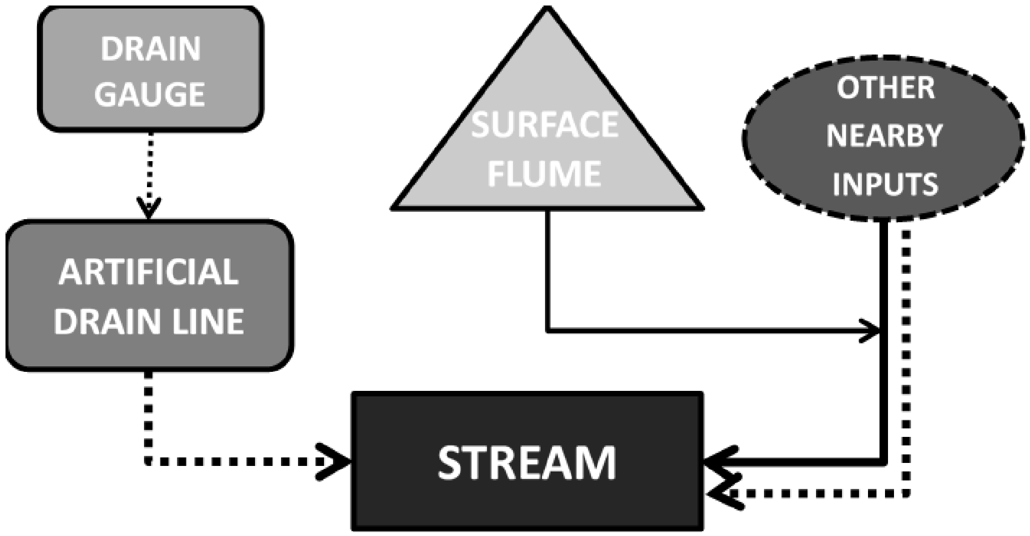


FIGURE 1.3. A conceptual model of the overall watershed sampling strategy for phosphorus that is proposed at the Cook Agronomy Farm which includes hand samples (when flow permits) of the drain gauge lysimeter, artificial drain, and surface flume as well as in situ measurements in the stream (Missouri Flat Creek) that drains the area. Dotted lines refer to subsurface flow and solid lines refer to overland flow.

To accomplish objective three, water samples were collected from two automated water samplers, one that collects surface runoff located at the base of the desired drainage catchment and one that collects subsurface flow at the artificial drain outlet in the SW corner of CAF. All samples were analyzed for DRP and subsets of samples were analyzed for total P. The difference between the two concentrations allows for quantification of inorganic and organic P. Information on temperature, electrical conductivity, flow rate, and discharge is also available. An in-situ phosphate sensor was installed during the 2015/2016 water year approximately 160 meters downstream from the main artificial drain at the corner of Whelan Rd. and Gray Rd.; the sensor location collects surface and subsurface flow from several nearby agricultural fields, including CAF. Speciation results from the water discharged from the artificial drain, soil-water extracts, and an in-situ drain gauge will be compared to understand P movement dynamics. Pore-volume break through analysis from soil core flow experiments were done to estimate P loading potential of the 12-ha subcatchment.

MATERIALS & METHODS

Site Background and Description

The R. J. Cook Agronomy Farm is a 57-ha dryland agriculture research site located on the Palouse landscape, within the NWRR, is owned by Washington State University outside of Pullman, WA, and operated in collaboration with the USDA-Agricultural Research Service. The farm has been involved in several large interdisciplinary research projects and has recently been designated as a Long Term Agroecological Research (LTAR) site by the USDA. The farm has operated under continuous direct-seed practices since 1998 following a typical three-year annual grain production rotation. Extensive soil and crop sampling at 369 locations across the site provide the basis for detailed research on spatial patterns of crop nitrogen use efficiency and exploration of precision agriculture management strategies. The CAF research site is currently included as a primary experimental research site for two large USDA research projects: Regional Approaches to Climate Change (REACCH) and the Site-specific Climate Friendly Farming (SCF) projects.

From 1981 – 2010, average precipitation was 520 mm/year, with most occurring during the fall and winter months as a mixture of snow and rain (WRCC, 2017). An estimated 14% of the subsurface water losses occur through an artificial drain line (with an additional 5% loss to deep groundwater, 1% to surface runoff, and the remaining 80% to evapotranspiration (E. Brooks, unpublished data)). Water flow from the artificial drain line is measured using a 1-inch Parshall flume at the outlet of a 12-ha subcatchment within the CAF (Figures 1.2 & 1.4), which is an estimation since the exact location of the artificial drain system is unknown. Using precipitation data, Keller et al. (2008) determined that it takes an estimated 150 mm precipitation to initiate flow to the artificial drain. A 13-year study on N fluxes from the artificial drain water suggest about 24% of the total precipitation is drained via the artificial drainage system (Kelley et al., 2017). A second 3-inch Parshall flume to collect overland flow is located within the catchment (Figure 1.2), but flow was limited and only observed during a few heavy rainfall events during the two-year study period, thus overland flow to Missouri Flat Creek is minimal. Event based water samples collected using automated water samplers were collected at each of these locations over the last three years, and were analyzed for electrical conductivity, pH, and nitrate concentration. Weekly grab samples have been collected and analyzed for nitrate from the artificial drain since 2000 (Keller et al. 2008).

The soils within this site are Mollisols in the Palouse-Thatuna series (USDA, 1978), with a bedrock geology of Columbia River Basalt flows (McDonald and Busacca, 1992). Large spatial heterogeneity exists at the site due to varying terrain and soil properties, especially with soil organic carbon (SOC), which has been shown to vary five-fold (Huggins and Uberuaga, 2010). A restrictive argillic layer is intermittently present across the field approximately 1-m below the surface (Figure 1.4), resulting in subsurface hydrology that is complex (Bellmore et al., 2015). Hourly soil moisture measurements are collected every 0.3 m down to 1.5 m throughout the site using 5TM sensors from Decagon Devices.

Mapped Restrictive Soil Layers

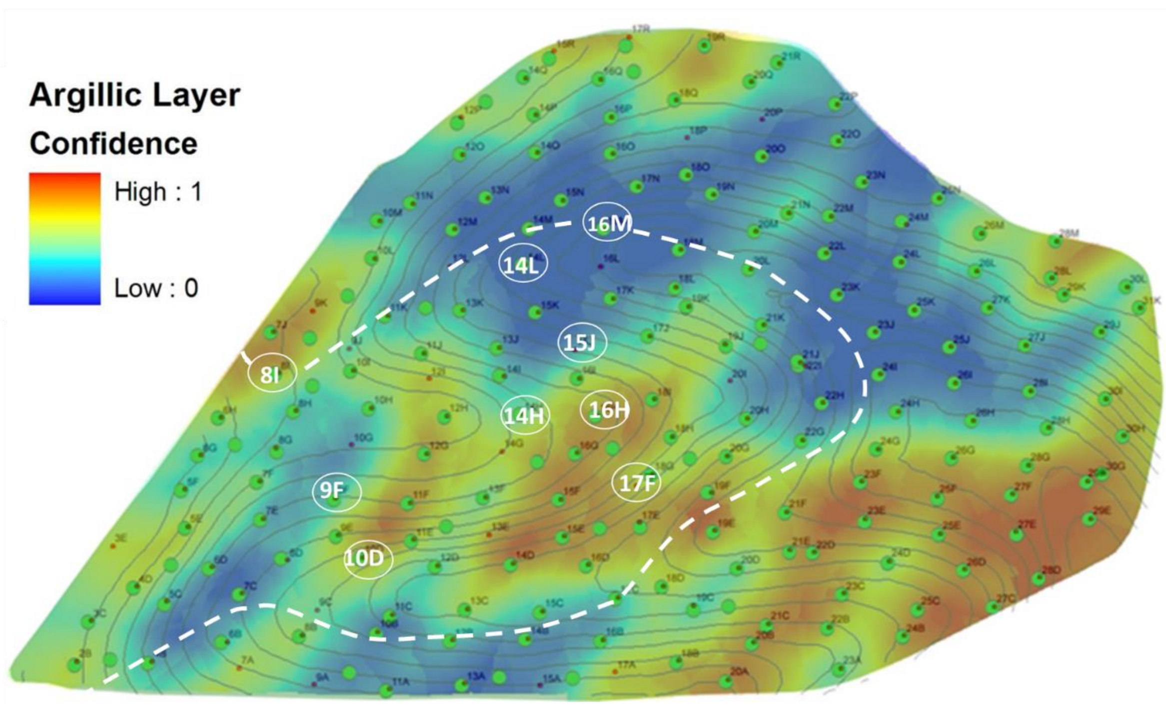


FIGURE 1.4. This map, created by D. Uberuaga (USDA-ARS) shows the relative probability that a restrictive argillic soil horizon exists within the 1.5 m of the soil surface at the main 57 ha no-till CAF field. A value of 1 gives the greatest confidence that a layer exists and a value of zero indicates that the layer does not likely exist. All available georeferenced sampling points and the nine sample points chosen for this study are identified on the map. The dashed line refers to the 12-ha subcatchment delineation estimated by Keller et al. (2008).

Water-extractable P from Soil Analysis

Nine sample points were chosen from the existing long-term monitored locations at CAF to represent varying topographic locations (Figure 1.4), three at the top slope (16M, 17F, 10D), three mid-slope (14L, 15J, 9F), and three lower slope points (8I, 14H, 16H). Points were also chosen to reflect variability in the presence of a restrictive argillic horizon throughout the field (Figure 1.4). Each point was tested at three of the sampled depths (0-10† cm, 20-30* cm, and a deep sample based on availability and soil horizon), and three years (1999*, 2008†, and 2015)

† Surface soil samples from 2008 were collected from the bottom of an organic “Duff” layer to the 10-cm depth (D – 10 cm)

* Mid-range soil samples for 1999 were only available based on horizon and chosen to contain the desired depth

Water-extractable P (WEP) on the soil extracts were prepared using a 1:10 solid solution ratio using deionized water following the protocol of Davis et al. (2009). The samples were mixed on reciprocal shaker at about 90-100 oscillations/minute for one hour and then filtered through a 0.45 µm polyether sulfone (PES) membrane filter. Phosphorus in the soil extracts was measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES). WEP (mg/kg) concentrations were converted to area-based WEP content by multiplying the respective bulk density for each point and year to obtain kg P per ha per 10 cm soil thickness. Averages were taken for all nine points for each depth and year and extrapolated to the 12-ha drainage catchment at the CAF for temporal analysis. Analysis of the first 30 cm was done by combining the WEP contents from 0-10 cm, 20-30 cm, and the average of the two values (for an estimated 10-20 cm value) to obtain kg P per ha for 0-30 cm.

Statistical analyses on the soil WEP results were completed using R version 3.4.1. Analysis followed a repeated measures two-way Analysis of Variances (ANOVA) approach to treat each point as an independent sample. A Tukey’s mean separation test was used as a post-hoc test to compare each depth subset (top, mid-point, and subsurface) and statistical inferences were based on a significance level of $\alpha = 0.05$. Correlation matrices were also created using R version 3.4.1.

Soil Core Study

Three undisturbed soil cores (two feet long and 10-inches in diameter) were extracted from the main CAF field, one each at a toe-slope, mid-slope, and top slope location, attempting to capture the spatial variability present in the field.

Two experiments were performed on these cores: (1) a rainfall simulation with varying rates of rainfall to help determine macropore activation, and (2) a ponded water experiment with a salt and P-spiked solution to compare P transport and sorption behavior through each column. The rainfall simulator is a portable model designed to mimic the relatively small rain droplet size and low rainfall intensity of the Palouse. For more information on the design, development, and mechanical specifications see Ullman and Bodah, (2011). The first simulation experiment was done to mimic a heavy rainfall event with an average rainfall rate of about 17 mm/hr for approximately three and a half hours and final applied water depth of 45, 52, and 38 mm rain for cores one, two, and three, respectively. After the heavy rainfall event, the cores were allowed to drain overnight, and a low rainfall intensity event was simulated with an application rate of approximately 6 mm/hr for about five hours and 45 minutes, or until it was believed that steady-state flow was achieved, for final daily rainfall application depths of 37, 25, and 30 mm for each respective core. Leachate was continually collected during the rainfall and draining periods in acid-washed bottles. The drainage rate from soil cores was determine by bucket and stop watch. 50-mL grab samples were taken on day two and analyzed for P concentration.

To compare core drainage behavior, applied rain and cumulative drainage were converted to pore volumes (L_{PV}) defined as the depth of water held in a specific soil profile having a length (L) between full saturation or porosity (p) and wilting point moisture content (WP).

$$L_{PV} = L \times (p - WP) \qquad \text{Equation (1)}$$

Since all cores were extracted in late-summer after grain harvest, it was assumed that the moisture in the soil was behind held at wilting point. Soil moisture was measured from small, intact soil cores taken during extraction. The average moisture content during soil extraction was determined to be 12.6%.

A ponded water experiment was completed using three 75-L Mariotte bottle drums (Figure 1.5) containing a solution of deionized water spiked with NaCl to an electrical conductivity (EC) of approximately 1,500 µS and orthophosphate to achieve a final concentration of 0.5 mg/L. The pH of the ponding solution was 5.7. Leachate volume was monitored using three pressure sensors and EC was measured continually using EC probes until each core drained the Mariotte bottle or emittance of leachate EC nearly matched initial ponding solution concentration. 50-mL subsamples were taken in varying time intervals based on rate of drainage. The samples were analyzed for DRP and EC within 72 hours. Subsample fill-time and final volumes were used to calculate flow rate. We were never able to achieve steady-state ponded conditions on the top slope core as the rate of drainage was nearly equivalent to the rate at which the Mariotte bottle could apply water to the core.

FIGURE 1.5. Ponded water experiment set-up with 20-gallon Mariotte bottles, pressure sensors, and EC probes in each respective drainage bucket.

Soil Core Image Analysis

After the cores had dried, a dye solution containing 1% by weight solution of blue dye was applied to each soil core. The dye solution was allowed to infiltrate vertically and the soil was excavated in one to two-inch increments to reveal dyed soil cross-sections, which were measured and photographed. The ratio of blue-dyed pixels to undyed pixels in each photograph was analyzed using the image analysis packages available in ArcMap (version 10.4).

Water Collection and Analysis

An auto-sampler (ISCO, Model 3700 or 6712, Lincoln, NE) located at the main artificial drain line outlet at the south-east corner of the CAF was used for water sample collection and set to collect event-based samples based on water stage thresholds, or weekly in the absence of a change in flow height. The changes in water depth in the flume was measured using a pressure sensor (INW, modelPT12, Kirkland, WA). Water temperature and the electrical conductivity of the drainage water was measured using a CS547-A probe (Campbell Scientific, Logan, UT). Water samples were initially analyzed for dissolved reactive phosphorus (DRP) by the colorimetric molybdate blue method (Pote & Daniel, 2009) with intermittent blank and quality check samples. Total DRP loads for each water year were determined using the LOADEST program (Version: MOD48) software available from the United States Geological Survey (USGS: https://water.usgs.gov/software/loadest). Total P was measured on 40 samples from 2016/2017 water year (Oct 2016 – June 2017) using persulfate oxidation method described in Pote, Daniel, & DeLuane, 2009 or by persulfate digestion at the Analytical Science Laboratory on the University of Idaho campus. An in-situ passive capillary drain gauge lysimeter (Decagon Devices) located upslope, northeast from the artificial drain outlet (Figure 1.2) was also sampled when water was present. A second ISCO water sampler was available on the no-till side of CAF to collect surface runoff at the base of the main drainage. However, mechanical issues paired with overall lack of flow to this specific device resulted in only four samples collected from the two years of this study.

During the 2016 spring runoff season, a HydroCycle-PO_4 sensor manufactured by Sea-Bird Scientific was deployed in Missouri Flat Creek from April 13th to April 29th, adjacent to Whelan Rd. (Figure 1.3) and approximately 600 feet west of the CAF artificial drain outlet. For the 2017 spring season, the HydroCycle-PO_4 sensor was installed directly at the artificial drain outlet. The sensor was set to sample at 6-hour intervals for both years. Grab samples that were laboratory tested were compared with sensor readings.

RESULTS

Water-extractable P at the CAF

WEP values for the soil samples from the nine geo-referenced points from the CAF were highly variable (Figure 1.6 and Table 1.1). In 2008, WEP increased in the surface soil samples at seven of the nine points as compared to 1999. A means separation test determined that the increase in the surface layer was significant ($\alpha = 0.05$) from 1999 to 2008 ($p = 0.001$) followed by a significant decrease ($p < 0.001$) from 2008 to 2015, but the overall change from 1999 to 2015 was not significant ($p = 0.643$). Year 2008 of the water-extractable P (WEP) data was somewhat of an anomaly for the surface soil. Seven out of the nine soil points show a large increase in WEP concentrations in the first 10 cm. From 1998 to 2009, a Great Plains no-till, double-disk drill with a leading fluted coulter to deep-band apply liquid fertilizer (including N, P, S) was used at the CAF. This drill was low disturbance, creating a build-up of a mulch (or also referred to as a "duff" layer), consisting of partially decomposed organic material. After harvest in 2009, site managers began to use another type of no-till drill, a Horsch Drill with Anderson hoe-type openers, that creates much more mixing of the surface layer and the excess mulch disappeared (Huggins, D. Personal communication. 2017, 13 October.). The increase in surface WEP in 2008 followed by a decrease in 2015 is most likely due to the build-up of this organic layer that was combated with a change in drill type. The increase in WEP for several points in 2008 is less noticeable when the WEP is converted to an area basis (Figure 1.7) because of the decreased bulk density, which likely occurred as a result of increased organic matter (Saini, 1966). The management change from 1999 to 2008 also led to slight behavioral differences for the mid-depth samples (mean increased) and to the subsurface (mean decreased), but these changes were not significant. A significant increase occurred in the subsurface from 2008 to 2015 ($p = 0.024$). Overall, from 1999 to 2015, WEP concentration in the surface soil increased in five of the nine points (17F, 8I, 15J, 14L, and 16M), and decreased in the other four points (10D, 9F, 14H, 16H). In the subsurface, only two points (14H and 14L) showed a decrease in WEP from 1999 to 2015, with the other seven having increased concentrations in the 16 year time-frame.

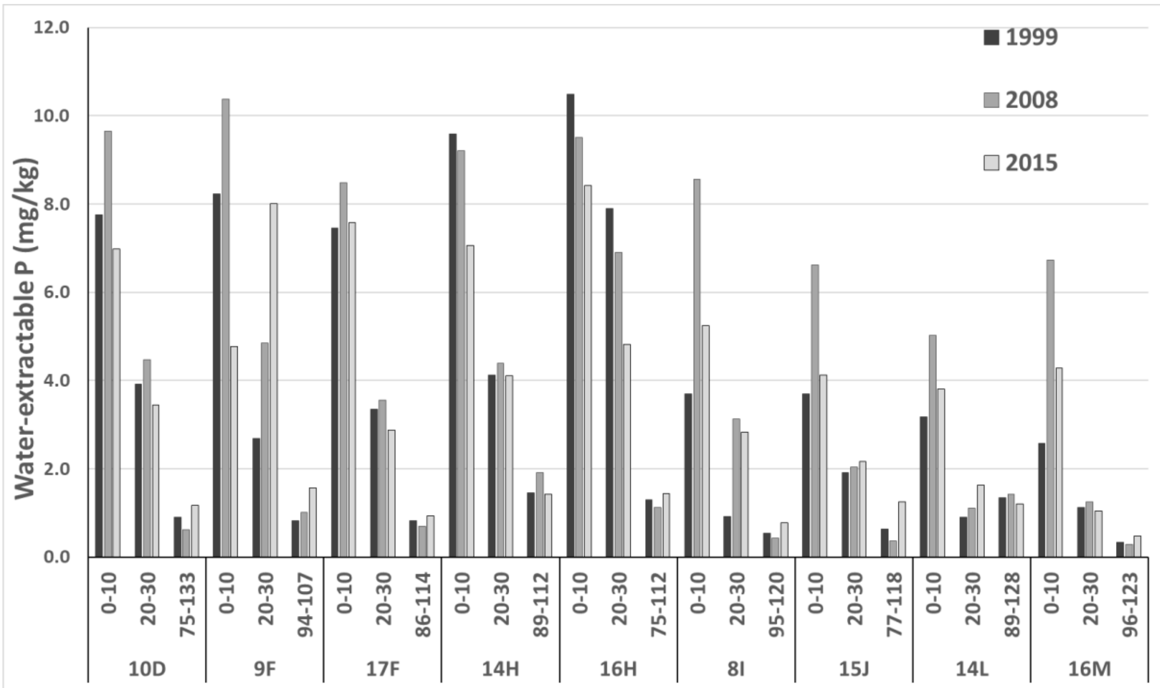


FIGURE 1.6. Water-extractable P (WEP) results for the nine sample points at three depths for 1999, 2008, and 2015 sample years. Surface soils for 2008 were sampled from end of duff layer to 10 cm (D-10). Mid-depth samples for 1999 vary based on horizon and were selected to capture desired depth.

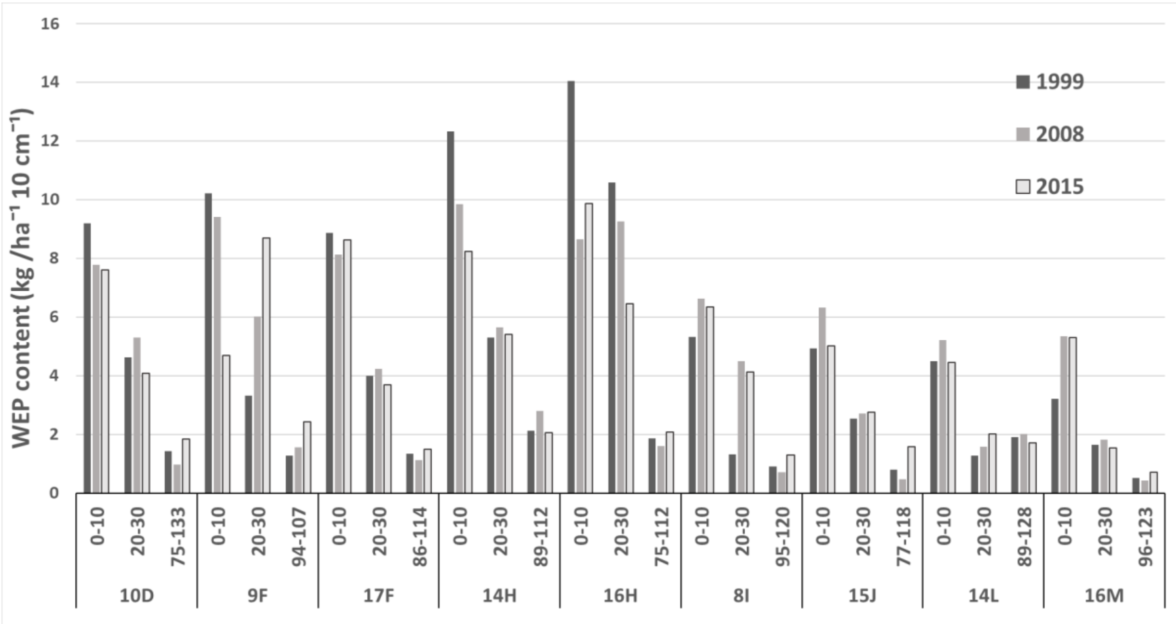


FIGURE 1.7. Soil WEP content (kg P/ha^{-1} per 10 cm) based on bulk density data for the nine sample points at three depths for 1999, 2008, 2015. Surface soils for 2008 were sampled from end of duff layer to 10 cm (D-10). Mid-depth samples for 1999 vary based on horizon and were selected to capture desired depth.

There was clear indication of redistribution of WEP from the surface soil to the deepest soil layer from 1999 to 2015 (Table 1.1 and Figure 1.8). Comparing average WEP contents from 1999 to 2015 (Table 1.1 and Figure 1.8), the average decreased in the surface layer, and increased in both subsurface depth samples. A means separation test comparison for top, mid-depth, and subsurface from 1999 to 2015 showed that the average WEP content increase in the subsurface was significant ($p=0.049$), whereas the decrease for 0-10 cm and increase for 20-30 cm sample depths were not significant ($p= 0.128$ and $p=0.709$, respectively). Standard deviations show a large spatial variability between sample points, so a repeated measures statistical analysis was used to treat each point as an individual sample for multiple observations, or years. This approach disregards landscape variation to analyze temporal change with greater precision (Ott & Longnecker, 2010).

TABLE 1.1. WEP (mg/kg) and soil WEP content (kg P/ha) averages of all nine points across the 12-ha drainage catchment for 1999, 2008, and 2015.

Year	Depth (cm)	WEP average (min-max) (mg/kg)	st dev	WEP content average (min-max) (kg/ha per 10 cm)	st dev
1999	**0-10**	**6.300** (2.582 - 10.490)	3.013	**8.06** (3.21 - 14.05)	3.78
	20-30*	**2.979** (0.898 - 7.903)	2.231	**3.84** (1.28 - 10.58)	2.91
	B-horizon**	**0.906** (0.337 - 1.449)	0.383	**1.35** (0.50- 2.12)	0.55
2008	**D-10ᵻ**	**8.240** (5.031 - 10.385)	1.751	**7.48** (5.21 - 9.85)	1.70
	20-30	**3.522** (1.110 - 6.911)	1.879	**4.56** (1.58 - 9.25)	2.39
	B-horizon	**0.872** (0.283 - 1.912)	0.543	**1.30** (0.42- 2.79)	0.78
2015	**0-10**	**5.809** (3.811 - 8.426)	1.715	**6.68** (4.45 - 9.87)	1.97
	20-30	**3.435** (1.041 - 8.014)	2.080	**4.31** (1.54 - 8.70)	2.26
	B-horizon	**1.137** (0.482 - 1.569)	0.350	**1.69** (0.72- 2.42)	0.50

*20-30 cm incremental samples were unavailable for 1999 so a horizon sample capturing desired depth was used
**Depth and thickness vary by point but remain constant for each year
ᵻ Surface soils sampled from end of duff layer to 10 cm

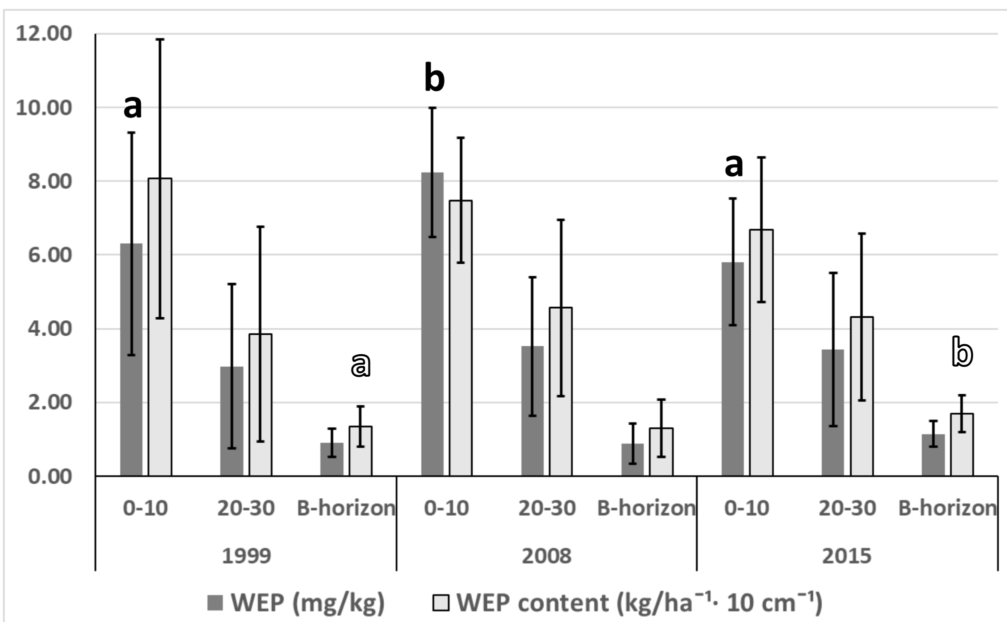


FIGURE 1.8. WEP (mg/kg) and WEP content (kg/ha^{-1}· 10 cm^{-1}) averages with standard deviation for the nine CAF soil points for 1999, 2008, and 2015. Values located in Table 1.1. Letters refer to significant differences (α= 0.05) using a means separation test and a repeated measures statistical approach.

Non-DRP concentration was determined as the difference between Total P and DRP. The percentage of WEP that is DRP ranged from 19% to 86% (Figure 1.9). Average percentage of total WEP that is DRP in the surface, mid-layer, and subsurface, are 62%, 42%, and 53%, respectively. This suggests that 38 to 58% of the water extractable P is present as a species other than DRP (i.e. orthophosphate). These other P species could be colloidal P or organic P.

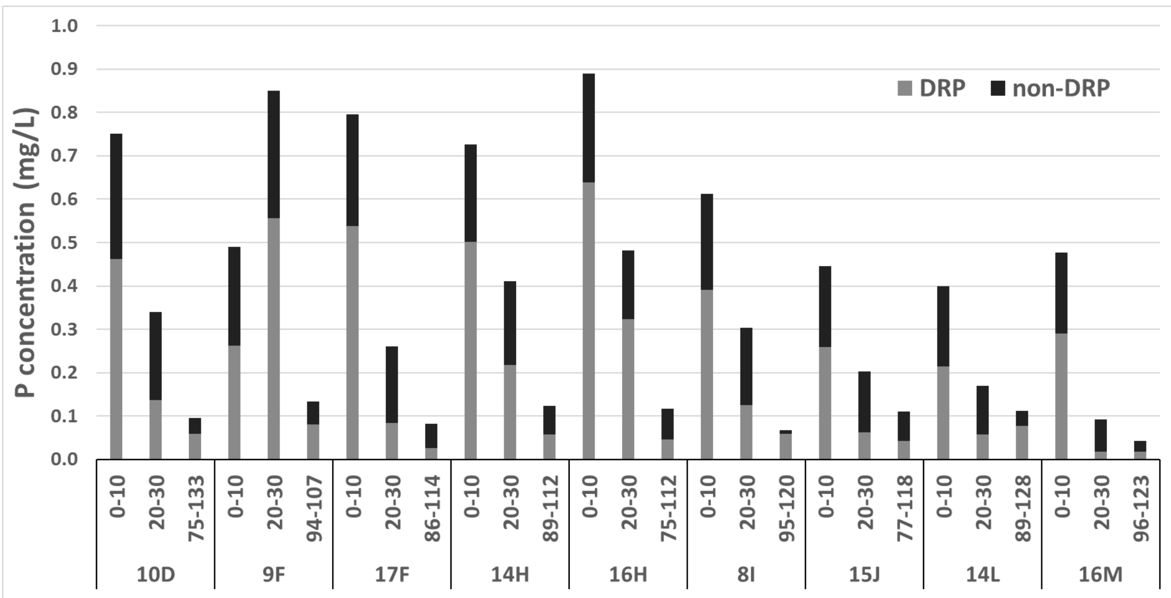


FIGURE 1.9. DRP and non-DRP results from the total WEP concentration for the 2015 sample year for the nine points at the three depths.

Macropore Network and Preferential Flow Pathways

The three large soil cores had very different hydraulic conductivities (Figure 1.10). The toe slope core took over 12 hours to drain the 75 L of ponding solution compared to the top slope core, which took less than three, resulting in a saturated hydraulic conductivity (K_{sat}) of at least eight times that of the toe slope.

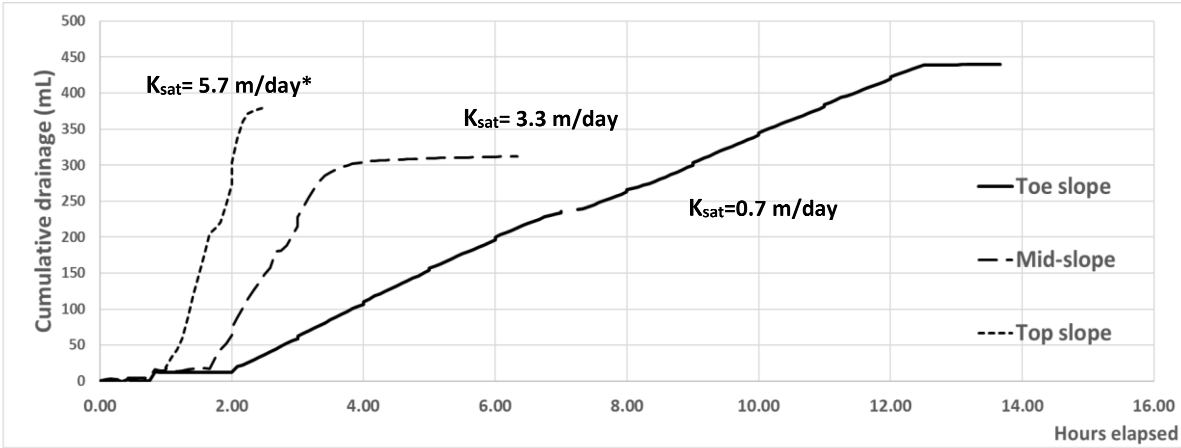


FIGURE 1.10. The cumulative drainage for each core and the resulting saturated hydraulic conductivity (K_{sat}) achieved under ponded conditions.

*Ponded conditions were never fully reached on the top slope core so this is likely an underestimation

Drainage results from the simulated high-intensity rainfall event (Figure 1.11) shows similar response rates for the toe and mid-slope cores, but a faster flow rate from the top slope core. The top slope core began draining very shortly after water application began suggesting macropore flow. The response to low-intensity rainfall event was very similar for all three cores suggesting the preferential flow may be dependent upon rainfall intensity. During the low intensity events, all the cores began draining before one pore volume was applied which can likely be attributed to the fact that the cores were still very wet from the high-intensity rainfall experiment which occurred on the proceeding day.

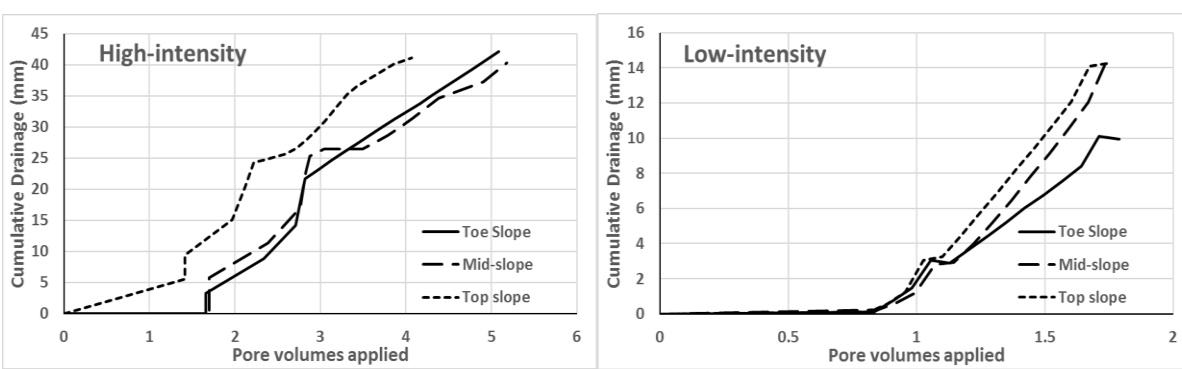


FIGURE 1.11. Cumulative drainage in mm for each core during the high-intensity rainfall event (~17 mm/hr) and the low-intensity event (~6 mm/hr).

The time-lapse results of the high-intensity rainfall event (Figure 1.12) shows the top slope core responded almost immediately after rainfall was initiated. Outflow from the core also declined the fastest after rainfall was terminated. The mid-slope and toe slope cores behaved similarly to each other.

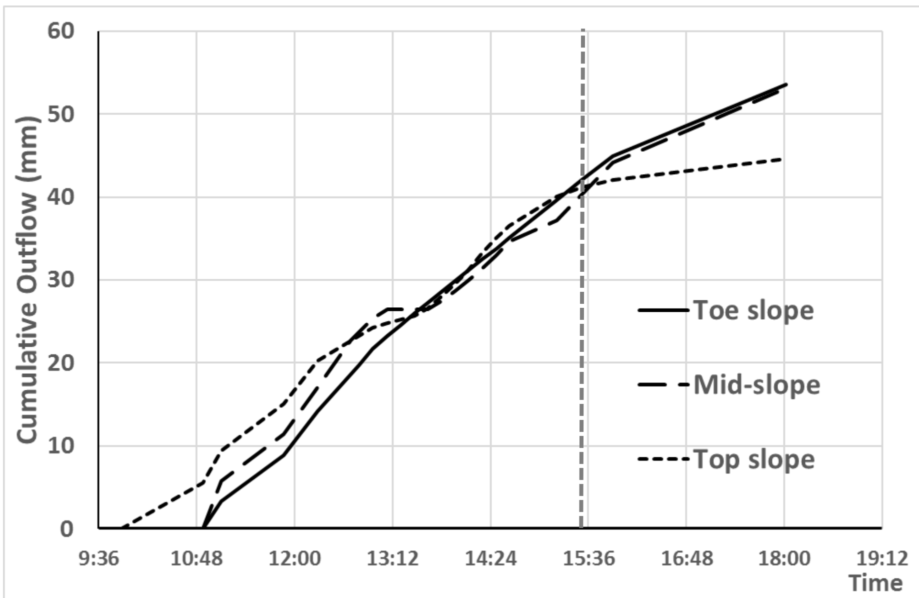


FIGURE 1.12. A time-lapse response of the outflow rate for each core during the high-intensity simulated rainfall event (~17 mm/hr). Rainfall was initiated at 9:53 and stopped at 15:31, indicated by the vertical dashed line.

Based on the downward progression of blue dye solution in the cores, all three soil cores exhibit preferential flow path networks. The blue dye also indicated that there is some degree of tortuosity in the preferential flow paths (Figure 1.13). At several depths below the soil surface the percentage of the soil cross-sectional area dyed blue increased with depth rather than decreased. This increased lateral dispersion of blue dye occurred between 5 and 22 cm below the soil surface in every core, however it was most prominent in the top and mid-slope cores (indicated by solid vertical arrows in Figure 1.13). An example of this is shown for the top slope core in Figure 1.14.

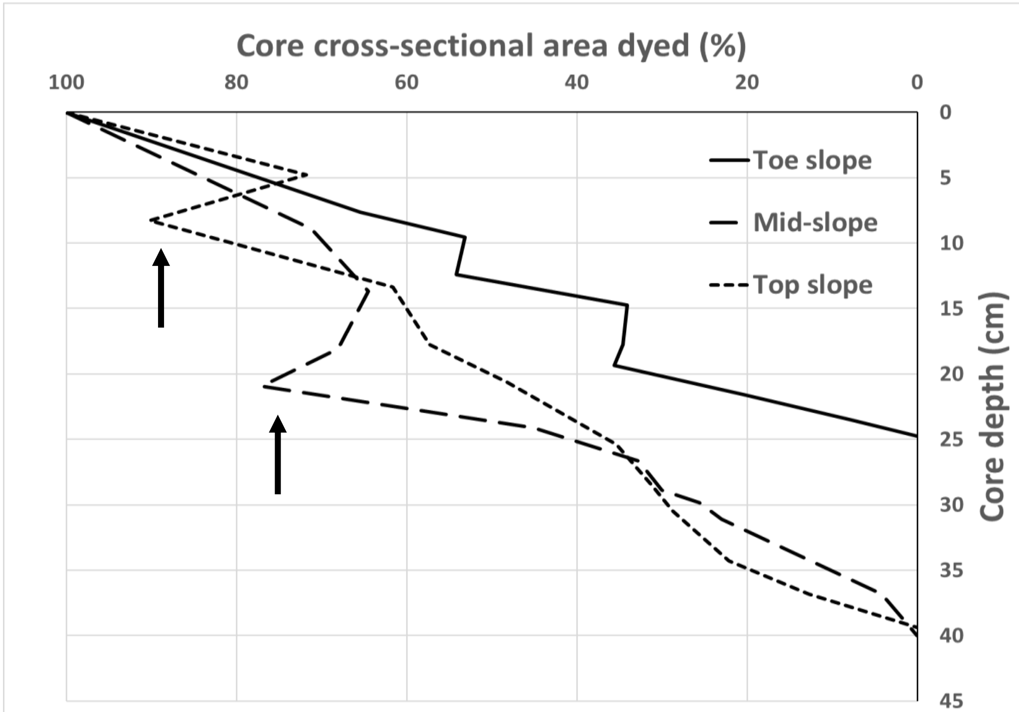
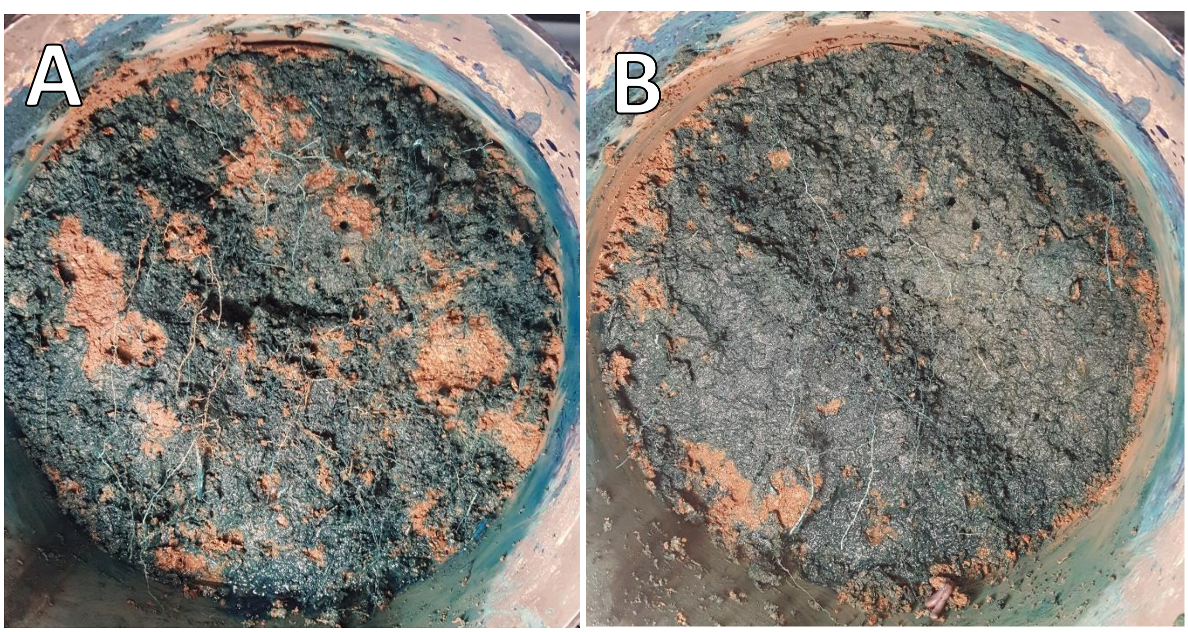


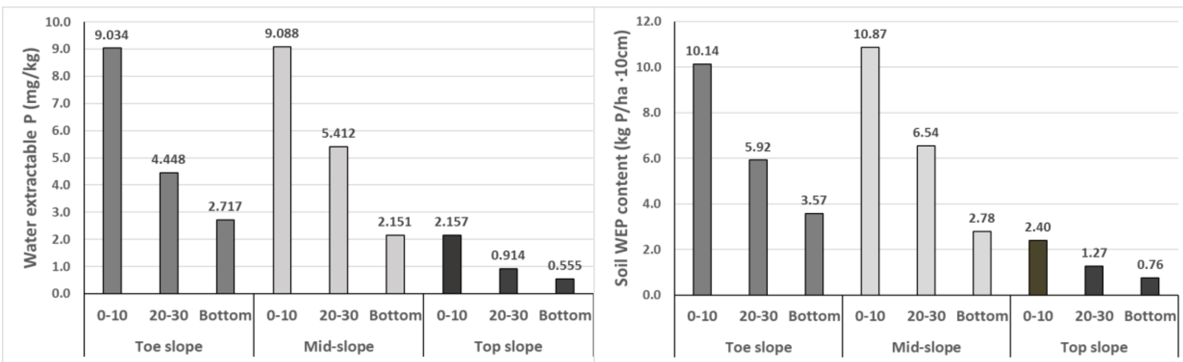
FIGURE 1.13. Image analysis results using ArcMap for each core showing the downward progression of dyed soil to undyed, bulk soil. Arrows show sharp contrasts between undyed soil above to dyed soil below.



FIGURES 1.14. Cross-sectional dyed core pictures at depths of 4.8 (picture A) and 8.3 cm (picture B) with approximated dyed areas of 72% (A) and 90% (B).

Phosphorus Response to Macropore Flow

The soil WEP concentrations taken from the excavated pit at the top slope core site (Figure 1.15 & Table 1.2) were less than one third the soil WEP concentrations in the other two cores. The toe and mid-slope cores had similar WEP concentrations that were greater than 2015 WEP concentrations measured from the nine points within the CAF subcatchment. Mid-depth (20-30 cm) values are also above the subcatchment mean of 3.44 mg/kg. In contrast, surface and mid-range depth soil WEP concentrations at the top slope location are lower than any of the nine field points. The subsurface WEP concentrations are greater than only one point (16M, 0.482 mg/kg).



FIGURES 1.15. WEP (mg/kg) and WEP content (kg P/ha per 10 cm) results for the three soil cores from soil samples taken during extraction at the three incremental depths.

TABLE 1.2. Soil core properties including estimated bulk densities, porosities, water-extractable P, and water-extractable P contents from soil samples taken during extraction.

Slope Position	Soil Type	Average Bulk Density (g/cm^3)	Average Porosity (%)	Depth (cm)	WEP (mg/kg)	WEP content (kg P/ ha· 10 cm)
Toe	Thatuna Silt Loam	1.26	52.6	**0-10**	9.034	10.14
				20-30	4.448	5.92
				Core bottom	2.717	3.57
Middle	Palouse Silt Loam	1.23	53.5	**0-10**	9.088	10.87
				20-30	5.412	6.54
				Core bottom	2.151	2.78
Top	Palouse Silt Loam (eroded)	1.29	51.2	**0-10**	2.157	2.40
				20-30	0.914	1.27
				Core bottom	0.555	0.76

Increased DRP in core leachate during rainfall simulation for the toe and mid-slope cores indicate a net loss of phosphorus from the soil cores, however the DRP concentration in the leachate from the top slope core was less than the DRP in the water added to the core (the applied building water had a DRP concentration of 0.015 mg/L) suggesting net adsorption of phosphorus (Figure 1.16). The largest pulse of P was observed in the toe slope core during the high-intensity rainfall event. A similar, smaller pulse was observed in the mid-slope core. The low-intensity event yielded small DRP flushes from the toe and mid-slope cores. The toe slope showed the greatest DRP fluctuations from the change in rainfall intensities.

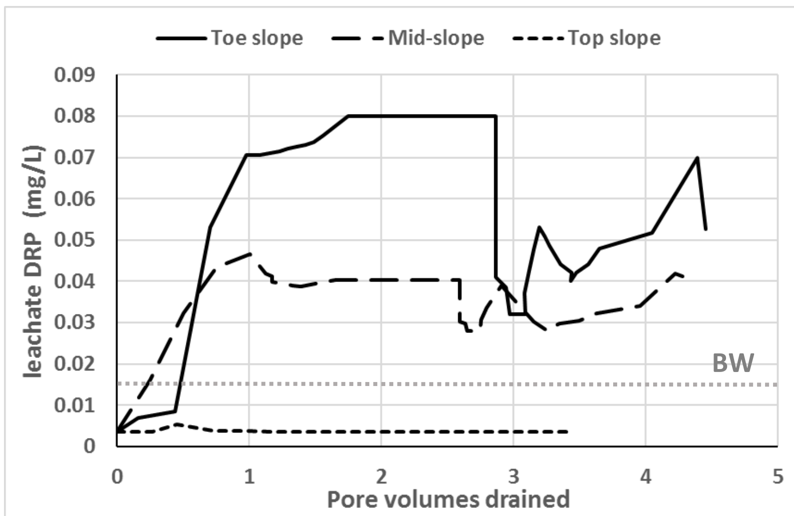
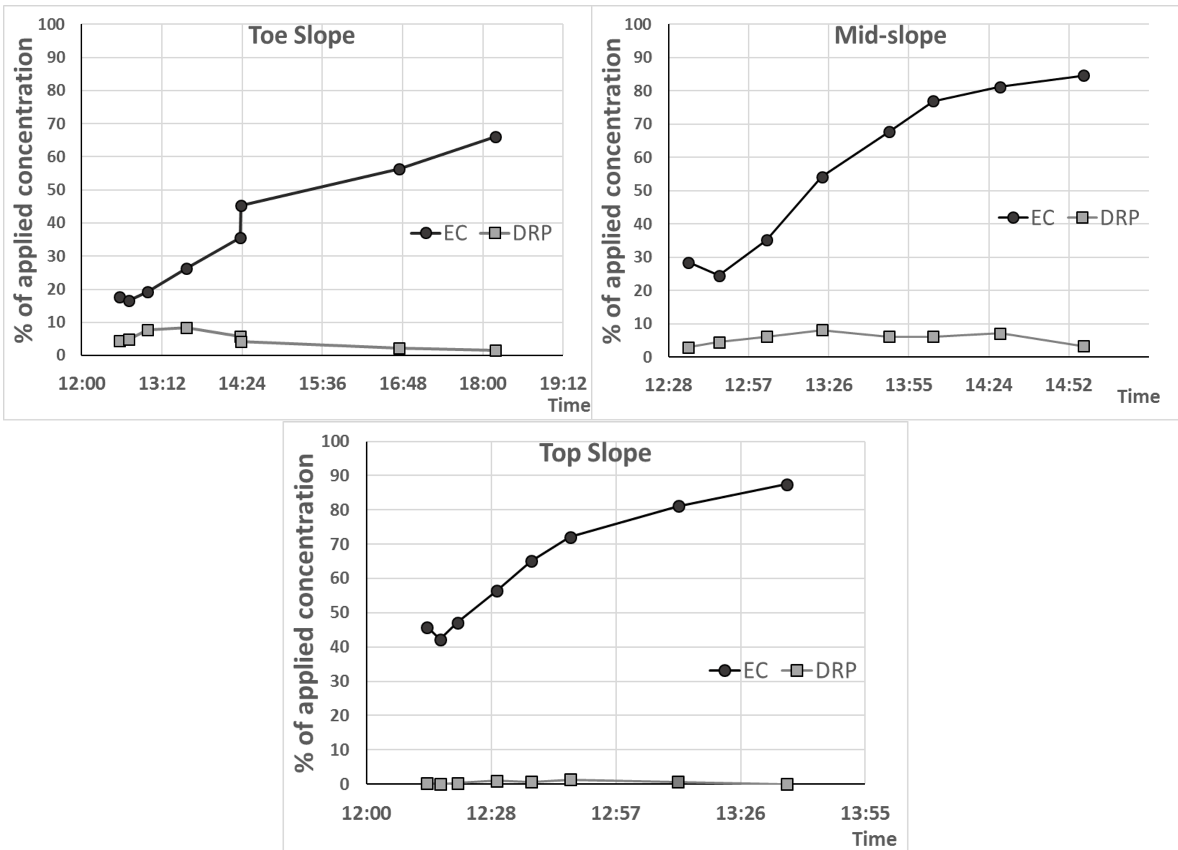


FIGURE 1.16. DRP concentrations (mg/L) in the leachate during simulated rainfall experiments. The dotted line marked "BW" refers to the DRP of the applied building water (0.015 mg/L). Sharp drop offs occurring at ~2.8 pore volumes for the toe slope and ~2.6 pore volumes for the mid-slope indicate the overnight break between high and low-intensity rainfall events.

All three cores exhibited strong P adsorption characteristics when the 0.5 mg/L ortho-P solution water was applied to each of the soil cores in the ponded water experiment. By the end of each of the ponded experiments, the EC in the leachate increased to nearly the EC of the applied water indicating that the pore water in the cores had been completely flushed. However, the DRP concentration in the leachate of all three cores never exceeded 10% of the amount that was applied (Figure 1.17). The top slope core showed the most P adsorption potential, with leachate values barely above the minimum detection limit (0.004 mg/L), and adsorbing more than 95% of the P from the influent solution.



FIGURES 1.17. Percentage of the 0.5 mg/L DRP and 1500 µS EC from the ponding solution that was emitted over time as the 75-L Mariotte bottle drained through each core.

Artificial Drainage Water and Stream Dynamics

The hydrograph for the 2015/2016 water year (Figure 1.18) shows that initial artificial drain flows, while providing minimal flow compared to the high flows of late winter and early spring, can transmit water with concentrations above the recommended TMDL limits. DRP concentrations spike during high flow events and exhibited a decrease in concentration over time during the spring runoff season. The majority of water samples have DRP concentrations above 0.05 mg/L. Concentrations plotted against discharge (Figure 1.19) show that the artificial drain behaves chemostatically; i.e., concentrations remain constant as discharge changes. This is represented by a log-log slope near zero, whereas a slope of -1 would indicate a dilution trend of fixed weathering fluxes (Godsey et al., 2009).

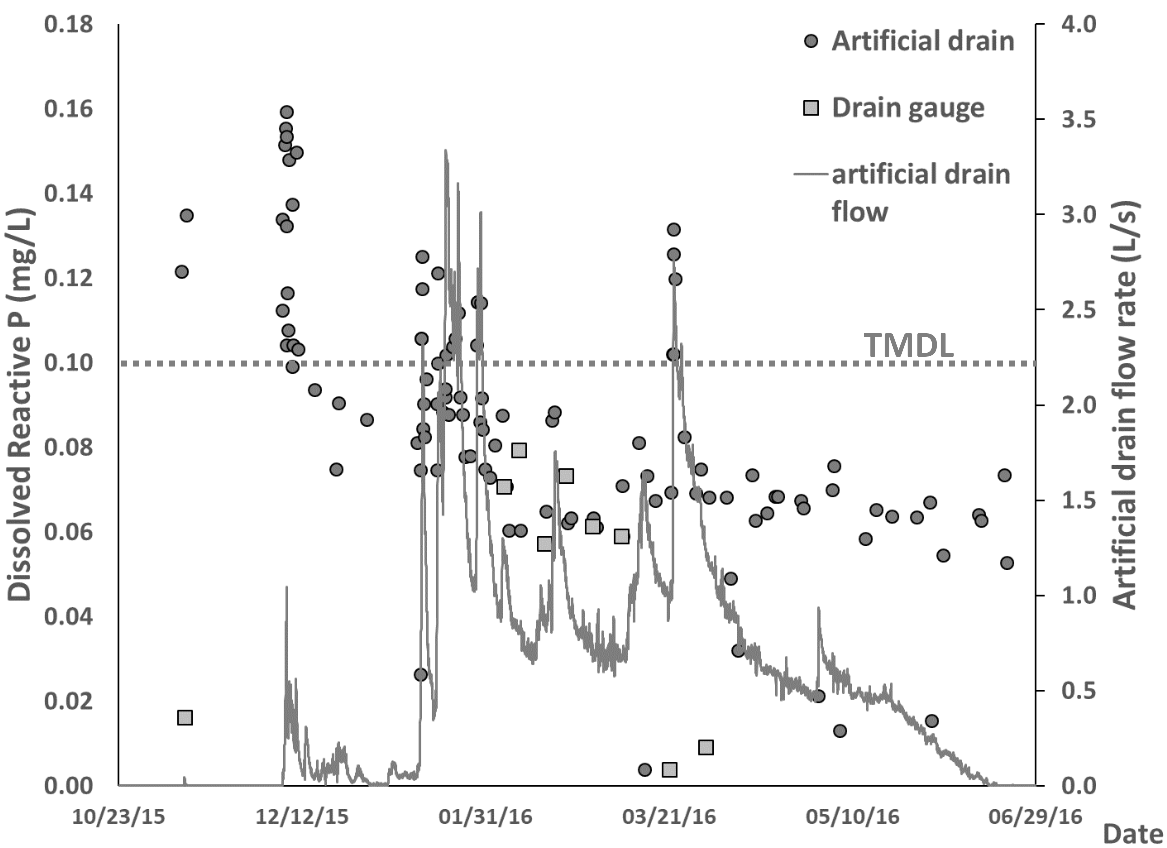


FIGURE 1.18. DRP results for the 2015/16 water year (WY) for the artificial drain and drain gauge at the CAF with artificial drainage flow rate in liters per second (L/s). The dashed line refers to the local TMDL for the Palouse River Subbasin (2005) and the Palouse River Subbasin (South Fork, 2007)(IDEQ, 2005, 2007).

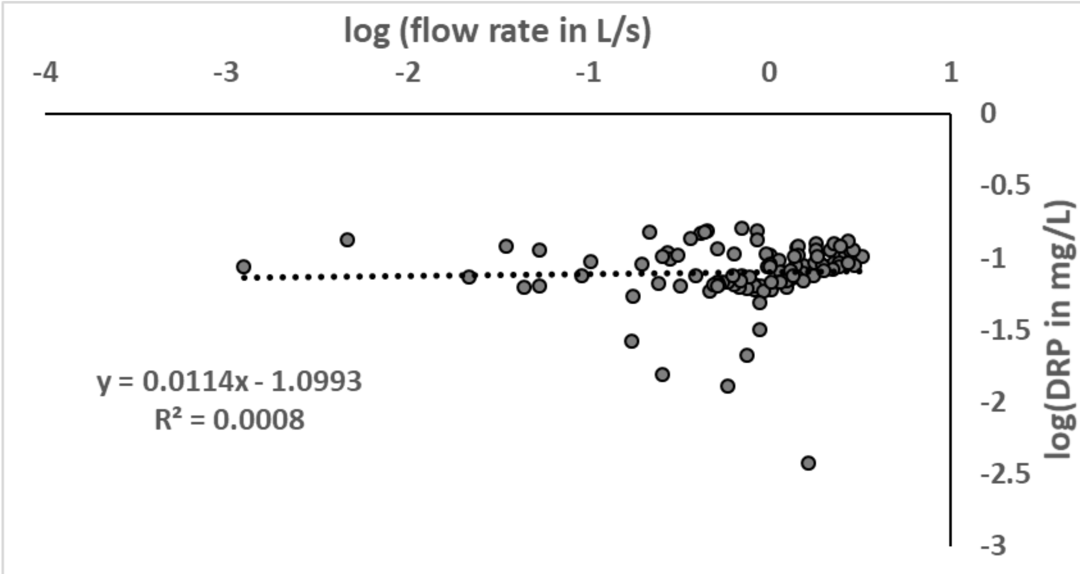


FIGURE 1.19. Log-log plot of DRP concentration vs. discharge at the CAF artificial drain for the 2015/16 WY with trendline equation and R-squared value.

Initial flush of water in the second year (Figure 1.20) had some of the highest DRP concentrations. The concentrations of DRP in this initial flush were comparable to the previous year (about 0.15 mg/L). The 2016/2017 season was much wetter than the 2015/2016 which resulted in increased flows however both years exhibited similar trends with the majority of discharge having DRP concentrations above 0.05 mg/L. Again, Figure 1.21 shows that the artificial drain behaves mostly chemostatically for DRP but more samples deviate from this trend. A subset of the samples analyzed for total P (Figure 1.22) also shows chemostatic behavior for TP during the second year with a log-log slope near zero.

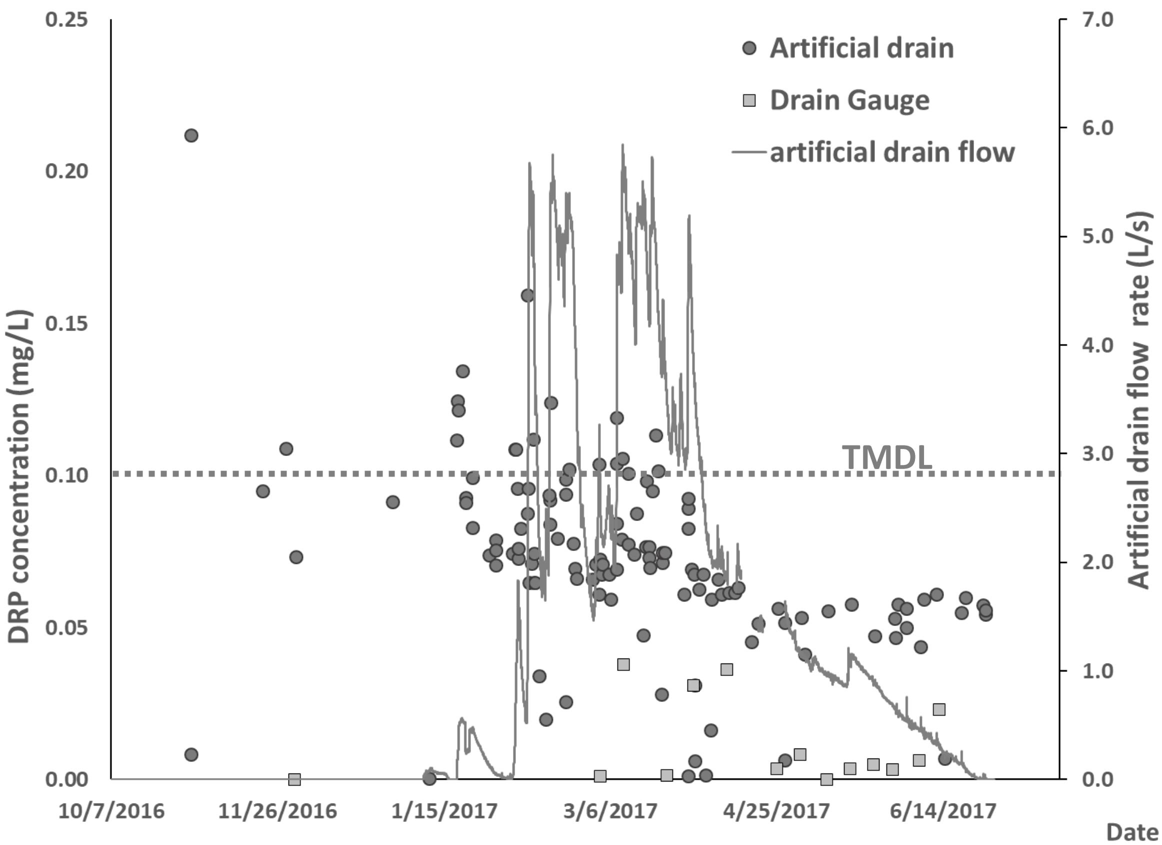


FIGURE 1.20. DRP results for the 2016/2017 water year for the artificial drain and drain gauge at the CAF with artificial drainage flow rate in liters per second. The dashed line refers to the local TMDL for the Palouse River Subbasin (2005) and the Palouse River Subbasin (South Fork, 2007)(IDEQ, 2005, 2007).

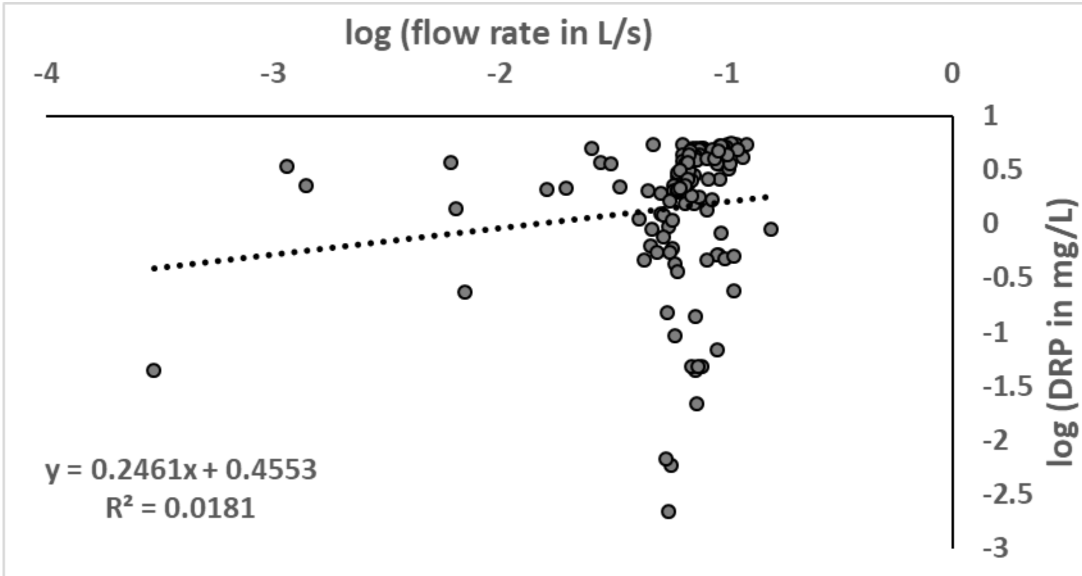


FIGURE 1.21. Log-log plot of DRP concentration vs. discharge at the CAF artificial drain for the 2016/17 WY with trendline equation and R-squared value.

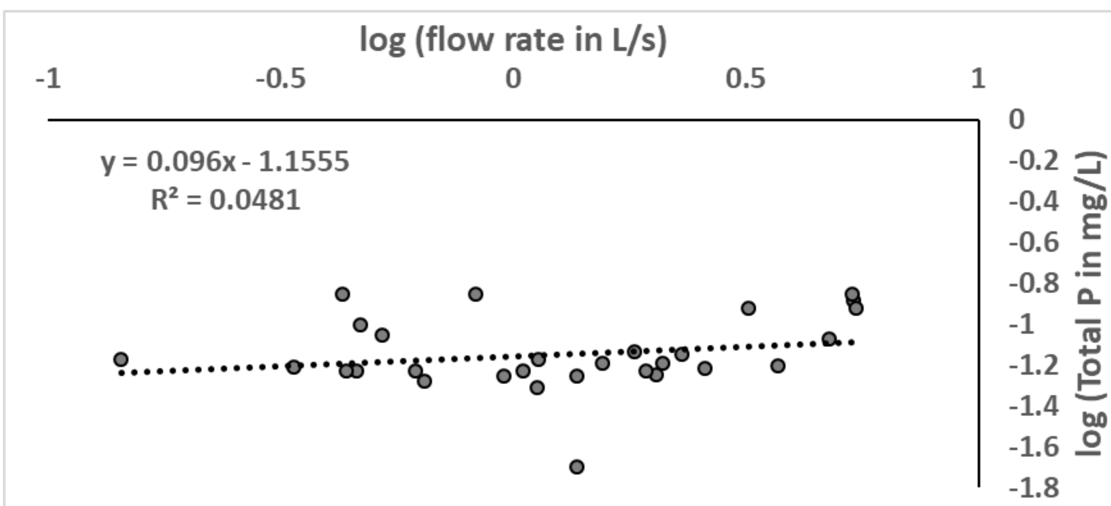


FIGURE 1.22. Log-log plot of total P concentration vs. discharge at the CAF artificial drain for a subset of the 2016/17 WY samples with trendline equation and R-squared value. Data supplied in Table 4.3 (Appendix).

TABLE 1.3. Surface runoff DRP results in mg/L for both sample years.

Sample date	DRP (mg/L)
1/17/2016	0.53
1/20/2016	0.39
2/14/2017	0.36
3/10/2017	0.33

Only four surface runoff samples, two from each water year, were collected during this study due to lack of flow and equipment error (Table 1.3). All samples are above the local TMDL recommendation of 0.10 mg/L.

Stream results during phosphate sensor deployment (Figure 1.23) show that DRP stream flow concentrations were similar to the DRP concentrations in the artificial drainage during the late spring runoff period. Diurnal fluctuations are evident in our data. Vandecar et al. (2009) noticed similar diurnal P fluctuations in wet tropical soils with decreasing bioavailable P occurring from 10:00 AM to 12:00 PM, which they attributed to biologic factors, such as microbial activity and plant respiration, that vary based on soil moisture, soil temperature, solar radiation, and other related factors. The lowest DRP concentrations in a 24-hr period noticed within Missouri Flat Creek typically occurred at the constant sampling time of 7:30 AM which could be due to a travel lag effect from the CAF since Vandecar et al. (2009) analyzed soil P directly and not stream dynamics.

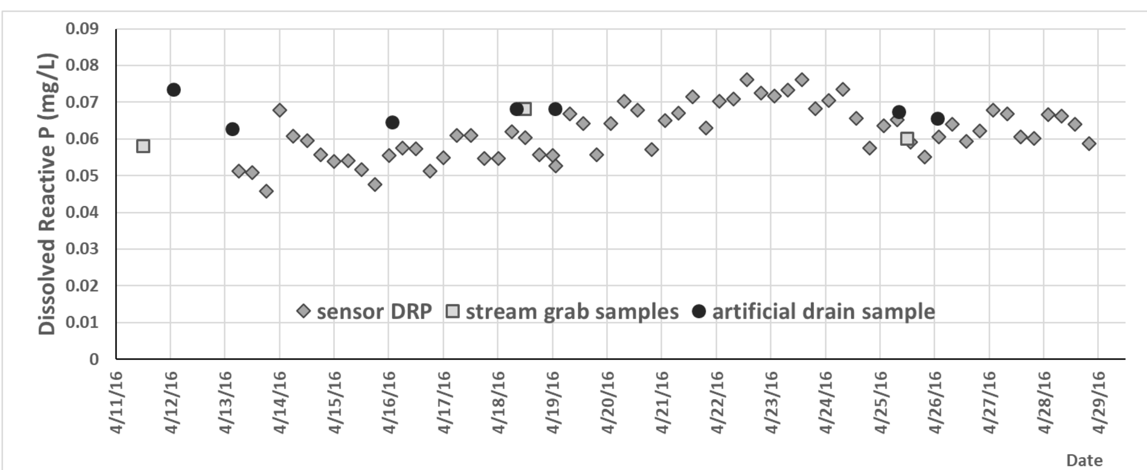


FIGURE 1.23. Phosphate sensor and lab analyzed sample DRP results for Missouri Flat Creek compared with lab analyzed artificial drain grab samples within the same time-frame.

In general, the water discharge from the artificial drain is composed primarily of dissolved reactive phosphorus (87% DRP) whereas the leachate from the drain gauge is largely non-dissolved reactive phosphorus (10% DRP), see Figure 1.24.

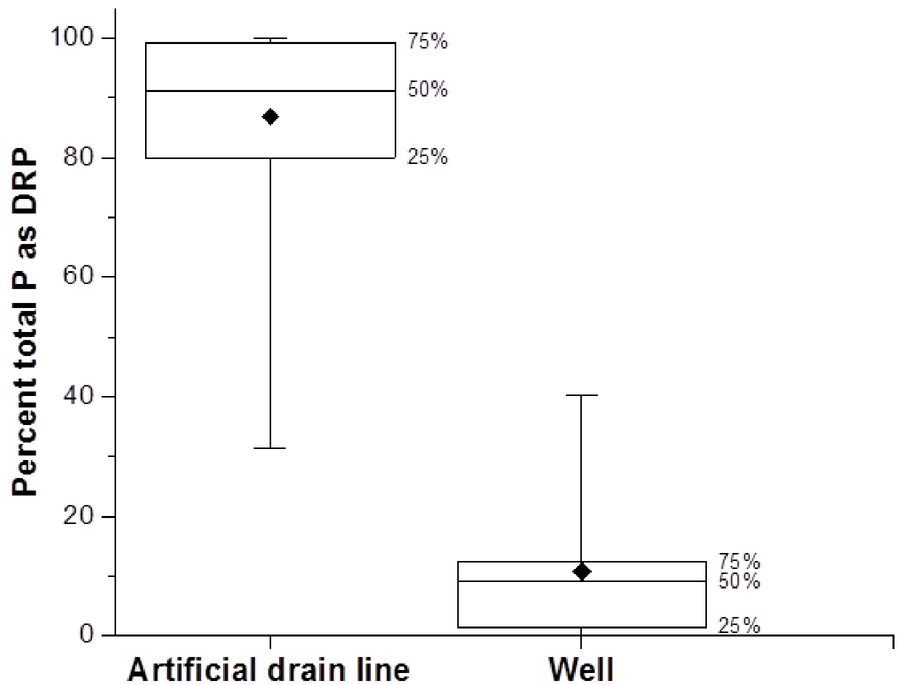


FIGURE 1.24. Speciation results for a subset of the artificial drain and drain gauge well samples during the 2016/17 season. Dates and concentrations located in Table 4.3 (Appendix). Diamond is the mean and the whiskers represent upper and lower quartiles.

DISCUSSION

Soil Phosphorus Dynamics

Water extractable soil P at the CAF has a highly variable spatial distribution, with results varying an order of a magnitude across the 12-ha drainage catchment. This agrees with the large surface spatial variability in acetate-extractable P previously observed at the CAF by Koenig (2007). Our data suggests that this spatial variability also exists at subsurface depths. Higher organic matter in a soil decreases bulk density (Saini, 1966). The lowest surface sample bulk density occurred in 2008, which corresponded it increased organic matter. The WEP spikes in 2008 may be from organically-bound soluble P species, which in turn led to an increase in the 2008 WEP concentration averages (Table 1.1) and combined WEP contents (Table 1.4). Relative crop yields (Figure 1.25) were also low for five of the nine points in 2008 which could have led to more soluble P species in the soil that weren't utilized by crops.

The overall field-scale trend is a loss in WEP content from 1999 to 2015 (Table 1.4). This does not necessarily equate to less P within the soil, but less soluble P species available for transport. Field average soil WEP (Table 1.1) and WEP content (Table 1.4) show an overall decrease in first 10 cm from 1999 to 2015 but an increase at 20-30 cm and subsurface over this time, suggesting a redistribution of water-extractable P species to the deeper soil horizons. Statistical analysis suggests that the subsurface has a unique response compared to the top 30 cm over this time period. The subsurface also experienced a slight increase in pH as opposed to the 0-10 cm and 20-30 cm depths which saw decreases from 1999 to 2015. Since P typically remains at the surface with little subsurface movement (Shah et al., 1975; Sims et al, 1998), a greater hydraulic connection to the deeper soil horizons from increased preferential flow pathways from no-till management could be facilitating the increase in WEP content at depth.

TABLE 1.4. Average WEP contents (kg/ha$^{-1}\cdot$ 10 cm^{-1}) of the three incremental depths for each of the nine sampled points for 1999, 2008, and 2015 with overall average WEP contents (kg/ha$^{-1}\cdot$ 10 cm^{-1}) by each sample depth. The total (kg WEP for the 12-ha catchment) for each year was calculated from the overall average WEP content of all nine points multiplied by the average maximum sampled depth (119 cm) and the estimated area of the drainage catchment (12-ha).

	Average WEP contents (kg/ha$^{-1}\cdot$ 10 cm^{-1})			
Sample point	**1999**	**2008**	**2015**	**± 1999 to 2015**
10D	5.08	4.68	4.51	-0.58
9F	4.94	5.66	5.27	+0.33
17F	4.73	4.49	4.60	-0.12
14H	6.58	6.10	5.24	-1.34
16H	8.83	6.50	6.14	-2.69
8I	2.51	3.95	3.92	+1.41
15J	2.75	3.16	3.12	+0.37
14L	2.56	2.94	2.73	+0.16
16M	1.78	2.52	2.52	+0.74
0-10 cm	8.06	7.48	6.68	-1.38
20-30 cm	3.84	4.56	4.31	0.47
B-horizon	1.35	1.30	1.69	0.34
Total (kg WEP)	**630.88**	**634.75**	**603.68**	**-27.21**

Four of the nine points show a decrease in WEP content from 1999 to 2015 (Table 1.4). Interestingly, the four of the five points that show an increase also have the lowest WEP content values. These four points show an increase in relative crop yield (Figure 1.25), which was also experienced by 10D and 17F despite a decrease in WEP contents. In fact, no relationship was found between relative crop yield and combined WEP contents (Figure 1.26) for the nine points for 2015 (R^2= 0.007).

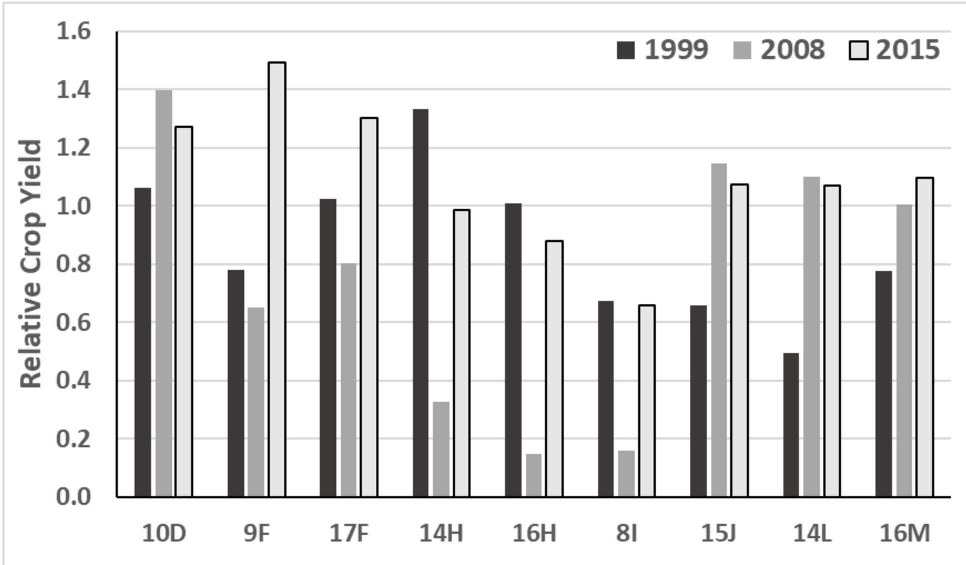


FIGURE 1.25. Relative crop yields for each of the nine CAF points for 1999, 2008, and 2015 as calculated by the USDA-ARS team. Previous CAF management divided the field into "strips" with each strip having a different history of crop rotation, fertilization rates, etc. Relative yield was calculated by normalizing the mean yield of a given crop collected from a given strip (Carlson, B. Personal communication. 2017, 17 November.).

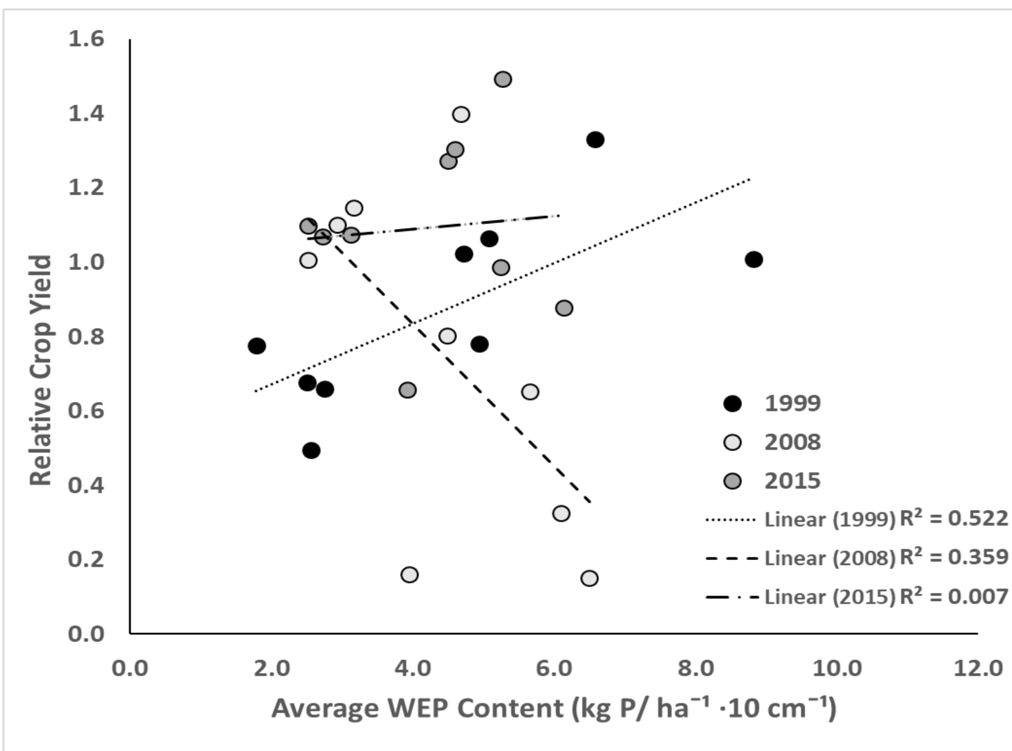


FIGURE 1.26. The relationship between combined WEP contents (Table 1.3) and relative crop yields (calculated by the USDA-ARS team) for each of the nine CAF points for 1999, 2008, and 2015.

Sample 8I shows the most significant increase in WEP content from 1999 to 2015, which did not contribute to an increase in relative crop yield (Figure 1.25). This point was planted as an alfalfa strip in past years. Alfalfa is a relatively higher phosphorus consumer compared to other crops grown in the area (e.g. wheat, chickpeas, canola)(NRCS, 2017), which could have led to the soil becoming depleted in P, allowing less for transport, resulting in a lower WEP value. 8I experienced the largest pH change (Table 1.5), dropping from 6.61 to 4.78 and 7.51 to 6.36 from 1999 to 2015 for the 0-10 cm and 20-30 cm depths, respectively. An increase in WEP for 8I agrees with our data, which show a negative correlation between pH and WEP values (Figure 1.27). Wang (2011) also found increasing P sorption with increasing pH values around our observed soil pH range. This is consistent with Zamuner et al. (2008), who found labile inorganic P negatively correlated to pH, but they also found that the no-till fields had significantly lower pH at the surface when compared to conventional tillage. They also observed a strong correlation between labile inorganic P with organic carbon, the latter which was significantly larger in the first 10 cm compared to conventional tillage. From available archived data (22/27 sampling points), only 6 samples show a decreasing organic carbon content, 4 of which were subsurface depths. As the organic carbon content is likely to increase at the CAF under no-till management (Unger and Huggins, 2014), this would theoretically lead to an increase in more soluble P species (Zamuner et al., 2008; Tiecher et al., 2012), which is contradictory to our observed overall loss in WEP content at the sampled sites. Correlations between WEP values show strong relationships with total percent carbon (Figure 1.28) and total percent nitrogen (Figure 1.29), with an increasing R-squared value from 1999 to 2015 for both.

WEP results have good correlations with several landscape attributes (Figure 1.30) with the best positive correlations occurring between soil nitrogen and carbon as well as upslope flow accumulation. Good reverse correlations were found between annual solar radiation, plan curvature, and soil depth (Figure 1.30). The occurrence of an argillic layer also seemed to be an influencing factor (Figure 1.4). The four points (14L, 15J, 16M, and 9F) that lack an argillic layer have an increase in total WEP contents from 1999 to 2015, suggesting that the better drained soils are becoming less depleted in soil P and have greater P adsorbing potential, increasing the amount of WEP they can contribute to solution.

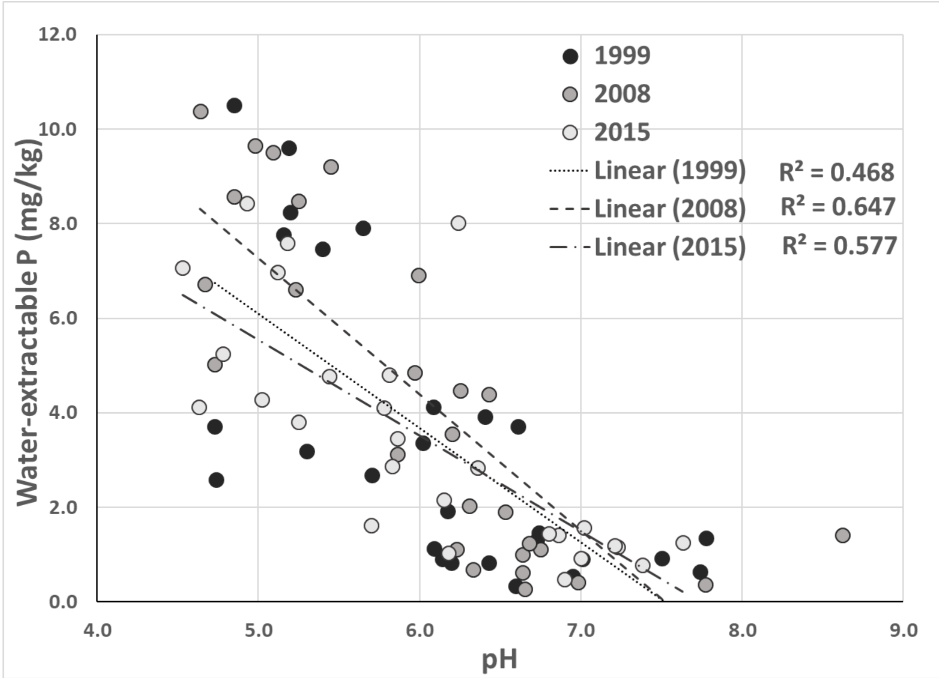


FIGURE 1.27. WEP and pH correlations for 1999, 2008, and 2015 with each respective R^2 value.

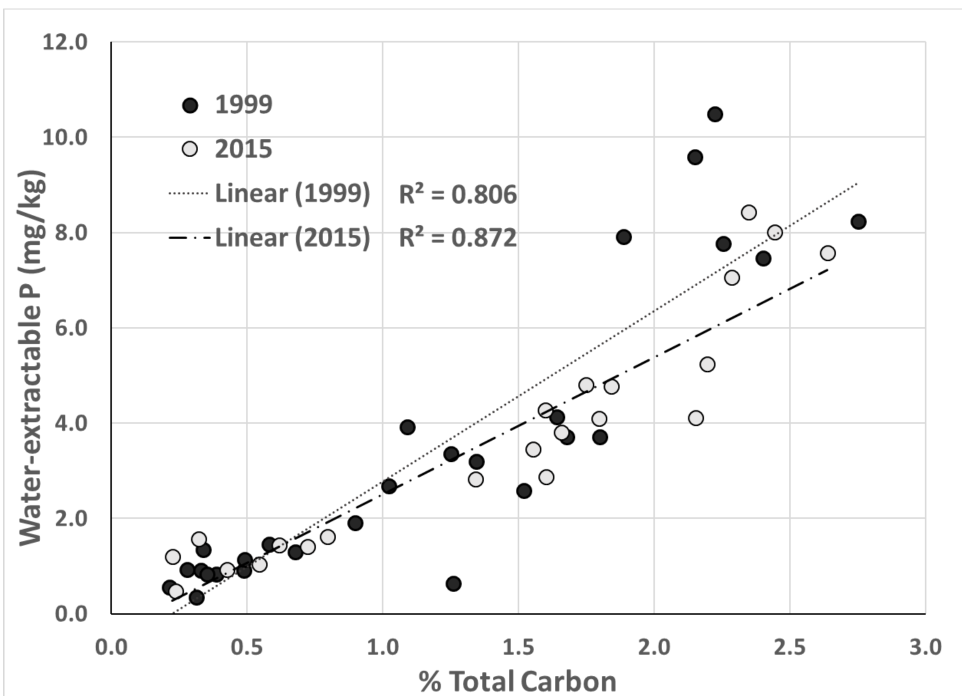


FIGURE 1.28. WEP and total carbon (%) correlations for 1999 (27/27 points) and 2015 (22/27 points) with each respective R^2 value. Year 2008 was omitted due to lack of data.

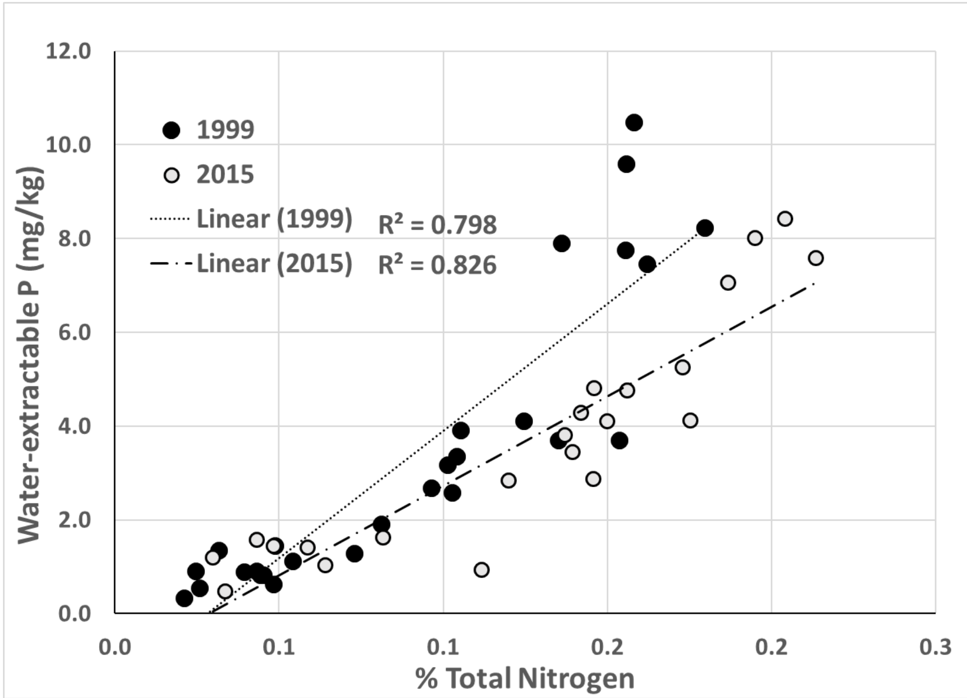


FIGURE 1.29. WEP and total nitrogen (%) correlations for 1999 (27/27 points) and 2015 (22/27 points) with each respective R^2 value. Year 2008 was omitted due to lack of data.

TABLE 1.5. Various soil properties for the nine sample points at the CAF for 1999, 2008, and 2015.

			1999			2008	2015		
sample name	**soil type**	**sample depth**	**pH**	**%Nitrogen***	**%Carbon***	**pH**	**pH**	**%Nitrogen***	**%Carbon***
10D		0-10	5.16	0.16	2.26	4.98	5.12	N/A	N/A
	Thatuna	20-30	6.41	0.11	1.09	6.25	5.86	0.139	1.553
		75-133	7.01	0.04	0.33	6.64	7.23	N/A	N/A
9F		0-10	5.20	0.18	2.75	4.64	5.44	0.156	1.843
	Staley	20-30	5.71	0.10	1.02	5.97	6.24	0.195	2.445
		94-107	6.20	0.04	0.39	6.64	7.02	0.043	0.323
17F		0-10	5.40	0.16	2.40	5.25	5.18	0.214	2.638
	Palouse	20-30	6.02	0.10	1.25	6.20	5.83	0.146	1.602
		86-114	6.43	0.05	0.36	6.33	7.00	0.112	0.427
14H		0-10	5.19	0.16	2.15	5.45	4.53	0.187	2.284
	Palouse	20-30	6.09	0.12	1.64	6.43	5.78	0.150	1.796
		89-112	6.74	0.05	0.58	6.53	6.86	0.059	0.724
16H		0-10	4.85	0.16	2.23	5.09	4.93	0.204	2.346
	Thatuna	20-30	5.65	0.14	1.89	5.99	5.81	0.146	1.749
		75-112	6.73	0.07	0.68	6.23	6.80	0.048	0.617
8I		0-10	6.61	0.14	1.68	4.85	4.78	0.173	2.195
	Thatuna	20-30	7.51	0.02	0.28	5.86	6.36	0.120	1.343
		95-120	6.95	0.03	0.22	6.98	7.38	N/A	N/A
15J		0-10	4.73	0.15	1.80	5.23	4.63	0.175	2.153
	Staley	20-30	6.18	0.08	0.90	6.31	6.15	N/A	N/A
		77-118	7.74	0.05	1.26	7.77	7.63	N/A	N/A
14L		0-10	5.30	0.10	1.35	4.73	5.25	0.137	1.659
	Staley	20-30	6.15	0.04	0.49	6.75	5.70	0.082	0.796
		89-128	7.78	0.03	0.34	8.62	7.21	0.030	0.226
16M		0-10	4.74	0.10	1.52	4.67	5.02	0.142	1.598
	Palouse	20-30	6.09	0.05	0.49	6.68	6.18	0.064	0.545
		96-123	6.60	0.02	0.31	6.65	6.90	0.034	0.236

*Measured on a Costech Elemental Combustion System 4010 elemental analyzer by the Dept. of Crop and Soil Sciences at Washington State University

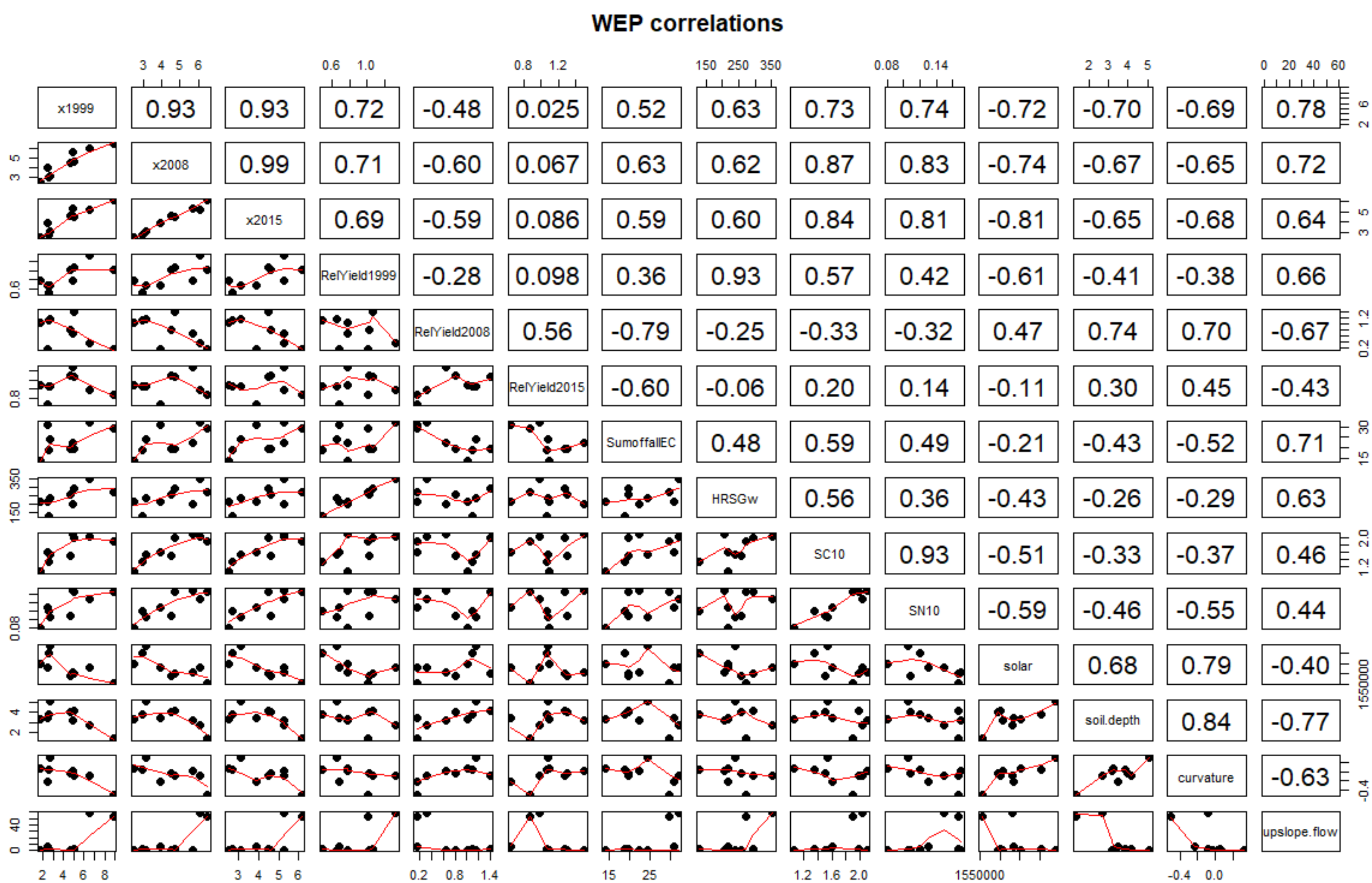


FIGURE 1.30. Correlation matrices calculated for average WEP contents (x1999, x2008, and x2015 values located in Table 1.4) and relative yields, sum of fall soil EC (mSm/m), Hard red spring wheat grain yield (g/m²), soil carbon content of the top 10 cm (SC10), soil nitrogen content of the top 10 cm (SN10), total annual solar radiation calculated from a 25m gridded map (kJ/m²/year), plan curvature calculated from a 30m gridded map, and upslope flow accumulation calculated from a 30m elevation map.

Macropore Network and Preferential Flow Pathways

The saturated hydraulic conductivity (K_s) results (Figure 1.10) of the three cores confirm findings by Brooks et al. (2004) that conductivities of the soils in this region can vary greatly from the reported values from the Soil Survey (NRCS, 2017), especially at a hillslope scale. Only the toe slope core with a K_s of 0.7 m/day was similar to the Soil Survey's reported values ranging from 0.4 to 0.8 m/day for soils in the area. The mid-slope (3.3 m/day) and top slope (at least 5.7 m/day) are at least four times greater than the reported K_s values. All three extracted cores from the CAF contained visible macropores that led to varying degrees of preferential flow as observed during simulated rainfall, ponded solution, and dye experiments. Drainage flow started almost instantaneous after a simulated heavy rainfall event (~17 mm/hr) for the top slope core, which had the highest K_s of the three. Drainage for the mid-slope and toe slope cores were similar and required more rainfall to initialize flow. When the high intensity event was stopped, flow rate from the top slope core decreased rapidly, which was less obvious for the other cores (Figure 1.12). This trend was not observed during the low-intensity event (~ 6 mm/hr) and all three cores had similar drainage when normalized by applied pore volumes (Figure 1.11). These findings suggest that preferential flow may be linked to rainfall rate as there was a difference in hydrologic response of the cores for the different simulated rainfall rates.

Image analysis of the dye tracer in the cores revealed that preferential flow paths exist, however there appears to be near surface restrictive layers that facilitate lateral redistribution of water and increased tortuosity (Figure 1.13). In many cores, within the top 20 cm, the percentage of dyed soil increased with depth (Figure 1.14). Plowing can cause a layer of compacted soil (plow pan)to develop at approximately 20 cm (SARE, 2012). We hypothesize that the plow pan acts as an impeding soil layer, creating lateral movement of soil water until an active flow path is found and water is allowed to continue subsurface infiltration. After this depth, flow was limited almost exclusively to pipe flow; however, not all observed macropores were hydraulically active (Figure 1.31).

FIGURE 1.31. Cross-sectional dyed core pictures at depths of 11 $\frac{3}{8}$ and 14 $\frac{1}{2}$ inch with estimated dyed areas of 30% and 4%, respectively.

Phosphorus Response to Macropore Flow

An initial pulse of P was observed from the toe slope and mid-slope cores after a simulated heavy rainfall event, which mimicked the behavior that was observed at the artificial drain for the CAF field during high flow events. However, despite having clear preferential flow the top slope did not exhibit any preferential transport of phosphorus. Interestingly, the top slope core showed the greatest potential in adsorbing P from solution even to the point of acting as a net sink for phosphorus transport. During rainfall simulation experiments, even with drainage starting almost instantaneously after rainfall was initiated and an input of 0.015 mg/L DRP from the building water, DRP concentrations of the leachate remained near the minimum detection limit (0.004 mg/L). The lack of P in the leachate can be partial explained by the low WEP in the soil profile at this upslope location. The WEP in the soil at this location was less than one-quarter of WEP at the other sample locations in the field and similar in magnitude to the deeper subsoil layers. This is in contrast to the toe and mid-slope cores which had relatively high soil WEP concentrations compared with the other sample locations in the field. It has been suggested that soluble P leaching is controlled by convective-dispersive transport processes, where the concentration of P in solution is inversely related to P adsorption in soil, requiring more flow volume to leach P from soils with higher adsorption potential (Shah et al., 1975). Using this approach, since the top slope core had an initially low WEP content, and thus less soluble-P species to contribute to solution, it's possible we did not simulate rainfall for a long enough period for noticeable P desorption to take place. Ponded water experiments took place after rainfall simulation so it's also possible we had already flushed the most available dissolved P species and created a system that was lacking in P which would more readily adsorb P from solution. Moreover, P desorption kinetics can vary greatly between soil types (Freese et al., 1995; Grant and Heaney, 1997). A similar study by Akhtar et al. (2003) found that preferential flow violated the typical convective-dispersive fluid transport processes during simulated rainfall events and instead caused instantaneous DRP spikes in the leachate. However, this study used simulated rainfall with 10 mg/L ortho-P and noticed an initial response of 4 mg/L in leachate due to preferential flow. Our simulated rainwater had a concentration of only 0.015 mg/L, so the maximum 40% emittance seen by Akhtar et al. (2003) would yield concentrations below the minimum detection level in our study.

In the ponded experiment, leachate DRP concentrations never exceeded 0.006 mg/L for the top slope core, even with the addition of 0.50 mg/L ortho-P spiked solution. An EC of 1,449 μS in the leachate was close to the influent EC (1,500 μS), indicating that leachate could not have been solely derived of initial pore water. These findings suggest that even with the highest degree of preferential flow and the ability to transmit water at a rapid pace through the profile, the soil at this location has a large ability to sorb P from solution at a rapid rate. Since we did not measure TP during core experiments, and with a relatively low solution pH used in the ponding experiment, conclusions made from flow experiments may carry uncertainty. However, similar results have been seen throughout the literature with McDowell and Sharpley (2003) finding that soils with low initial P contributed very little to solution. Since our top slope core had the lowest overall WEP of any soil in our study, and we had already subjected this core to rainfall simulation, it is possible we stripped all P species readily available for leaching, depleting available P. Akhtar et al. (2003) found that the cores with the highest preferential flow also had the highest adsorption coefficient. However, this did not inhibit P breakthrough, which they saw in all cores during their ponded flow experiment with some degree of preferential flow in all. Recovery of DRP in leachate in our study was less than 10% for all three soil cores (Figure 1.17), with barely noticeable P breakthrough. Lateral dispersion exhibited in the dye experiments (Figure 1.13) may have allowed for increased contact with the soil to facilitate the necessary adsorption required to eliminate any peak P response in the leachate. Lack of P breakthrough may also be a function of slow P movement (Shah et al., 1975; Sims et al., 1998) and relatively low P in the ponding solution compared to that of Akhtar et al. (2003).

Artificial Drainage Water Results and Watershed Dynamics

Overland flow during the time period of this study only occurred at a few events, and therefore, even though samples had elevated concentrations of DRP (Table 1.3) in relation to the artificial drain, the surface runoff is not a major contributor to P loading. It has been estimated that surface runoff comprises only 1% of the total water mass balance leaving the CAF compared to the 14% (E. Brooks, unpublished data) to 24% (Kelley et al., 2017) loss to subsurface artificial drainage. Even though surface runoff most likely only poses a threat to the nearby stream for a short duration of the runoff season, typically if the soil is frozen and/or conditions promoted large amounts of overland flow, immediate action should be taken to prevent this water rich in particulate and dissolved P varieties from entering the streams.

The artificial drain discharge only exceeded nearby watershed TMDLs (0.1 mg/L TP) for short intervals throughout both seasons. But the overwhelming majority of artificial drain DRP was above 0.05 mg/L, especially during the 2016/2017 runoff season, which was an unseasonably wet year for the area. With constant seasonal flows, and a direct pathway for dissolved P to enter the Missouri Flat Creek, the amount of P lost can be substantial. Using the LOADEST program (https://water.usgs.gov/software/loadest/), we estimate the DRP load at 1.06 kg P (0.09 kg/ha) and 1.80 kg P (0.15 kg/ha) for the 2015/16 and 2016/17 runoff seasons, respectively, for the estimated 12-ha drainage catchment at the CAF. This DRP loading rate is less than loading rate observed from 8-years of artificial drainage data for the Upper Big Walnut Creek watershed in Ohio, USA (King et al., 2015) where DRP loads ranged from 0.22 to 0.69 kg/ha (mean of 0.39 kg/ha). However, our observed DRP load is greater than that found by Smith et al. (2015) who reported a median artificial drain soluble P load of 0.03 kg/ha for four artificially drained fields over a 6-year period in the St. Joseph River watershed located in Indiana, USA.

Using the two-year average P load for the subcatchment of 1.43 kg P (0.12 kg P/ha) would result in an estimated 6.8 kg P lost in the form of subsurface drainage from the entire 57-ha field.

An estimated 24% of the annual average precipitation (we used the 29-year average, 520 mm (WRCC, 2017)) is drained by the artificial drain (Kelley et al., 2017) each year, which equates to about 125 mm transported to the artificial drain. A more conservative subsurface water loss number of 14% of the annual CAF water budget from Brooks (unpublished data) would suggest only about 73 mm of precipitation is transported by the artificial drain. Our cores received an average of 143 mm of precipitation and drained an average of 85 mm during simulated rainfall events, which would be similar to an entire year worth of artificial drainage. We did notice initial DRP spikes in the toe and mid-slope cores, which is similar to what is observed in the artificial drain discharge.

Although the P transport observed in the artificial drain exhibits clear preferential behavior, the ponded core experiments suggest that preferential transport of ortho-P is minimal. The average distance of about 120 cm to the artificial drain from the surface (Shults, unpublished, 2017) equates to about 2.1 pore volumes of water. During the ponded experiment we drained our cores an average of 7.1 pore volumes, or about 3.5x the pore volumes experienced in a typical year at the artificial drain line. This suggests the artificial drain line would experience even less transport of P than observed in the soil core experiment. However, the export of P from the artificial drain line is greater than predicted from the core experiment, suggesting a major disconnect in our P loading knowledge. Despite applying more water to a soil core than would be experienced by soils at CAF in more than three years, less than 10% of DRP was recovered in leachate as observed from the artificial drain line. This is compared to the phosphorus concentration in the artificial drain water that can be well above the recommended 0.1 mg/L TP TMDL, especially at the beginning of the runoff season. This suggests that soils at this site have the ability to sorb P from solution at a rapid rate and that there are likely more localized sources of phosphorus within the field that can contribute preferential flow to the artificial drain. These sources will likely have large soil WEP potentially in organic rich environments. Stream results show little dilution occurring at the end of the runoff season as multiple sources of flow enter Missouri Flat Creek, but it did not exceed the nearby TMDL during the monitored timeframe. However, only DRP was measured in stream water and the local TMDL represents the suggested limit for TP.

An initial high concentration of DRP at the beginning of artificial drain flow with the first winter flow could be due to the flushing phenomenon that was observed by Keller et al. (2008) when studying nitrate in the artificial drain located at the CAF. Kelley et al. (2017) describes this behavior as chemostatic, or that the nitrate fluxes are correlated with water fluxes, suggesting that the system is transport limited and a large pool of dissolved nitrate exists that is primed for release when winter-spring flows commence. In fact, sample concentration compared to instantaneous discharge (Figures 1.19, 1.21, & 1.22) confirm that the artificial drain behaves chemostatically, or that concentrations remain constant with a change in discharge rates (Godsey et al., 2009), suggesting that DRP is transport limited. A similar flushing phenomenon explained by Keller et al. (2008) and Kelley et al. (2017) was observed for P at the CAF as initial winter flows prompted the largest observed DRP spikes at the artificial drain for both seasons. Lam et al. (2016) observed initial spikes of DRP from reduced tillage sites that decreased after consecutive rainfall events. Concentration of DRP in flow decreases as the growing season commenced and crops began to use the dissolved P in soil water stores, allowing less for subsurface transport. High flow events prompted DRP spikes, which is similar to other studies comparing artificial drain P flows to preferential transport (Lam et al., 2016; Macrae et al., 2010; Macrae et al., 2007). Artificial drain flow observed by Lam et al. (2016) in the Ontario, Canada, were similar to our study site, and the Palouse in general, which is largely seasonal and the greatest response occurring from snowmelt and rainfall events. DRP percentage in terms of TP observed by Lam et al. (2016) ranged from 8% to 73% (typically below 50%) with the larger ratios occurring during the autumn and winter months. From the literature, sandier soils typically display lower %DRP to TP compared to soils with higher clay contents (Tan and Zhang, 2011; Eastman et al., 2010; Heckrath et al., 1995) but the opposite has been observed as well (Beauchemin et al., 1998; Macrae et al., 2007). Specifically, Macrae et al. (2007) observed varying DRP% from loam and silt loams that peaked at 50% – 55% during the winter months to <20% later in the growing season. The CAF artificial drain, however, averaged 87% with no noticeable seasonality change. Djodjic et al. (1999) suggests that dissolved P moves more readily through "dead-ended" macropores due to diffusion than particulate-P which is bound to particles. This could explain the relatively high DRP% because dye experiments show patchy and highly variable flow pathways through the profile.

The artificial drain water phosphorus speciation was different than the leachate from the drain gauge, which averaged 11% DRP. Previous experiments performed on the drain gauge suggest preferential flow is the main contributor to sample water (Payne et al., 2012). Soil-water extracts show the average percentage of DRP to non-DRP are 62% for the surface, 42% for the mid-depth, and 53% for the subsurface. The lack of natural soil aggregation creates more surface area, allowing previously isolated P-species to solubilize. The lack of DRP in drain gauge water could be solely due to lack of soil P available for potential to leach and low residence time as we saw in the extracted top slope core but without data to support this, only inferences can be made. However, the drain gauge does show the ability for preferential flow pathways to move non-DRP species, which is an important finding and agrees with findings from Bellmore et al. (2015).

TABLE 1.6. A summary of important findings and unresolved issues for the Cook Agronomy Farm.

	SOIL	FLOW EXPERIMENTS	TILE LINE
Preferential flow pathways (PFPs)	• PFPs evident • Causes varying Ks through the profile • Transport of non-DRP	**Macropore flow** →	• DRP spikes with high flows • Non-DRP higher earlier in runoff season
Phosphorus behavior	• Widely variable WEP contents • Average of ~52% DRP:TP • Some soils have high retention capacity	**DRP source?**	• Majority of flow DRP >0.05 ppm • DRP:TP >80%

Table 1.6 describes the disconnect between P movement through the soil profile and the resulting DRP loading at the artificial drain. A plausible explanation for the large amount of DRP in artificial drain flow was explained in depth by Kelley et al. (2017) when studying nitrate movement. They suggested that a large pool of dissolved nitrate accumulates after the growing season from mineralization of crop residue and fertilizer inputs. Preferential flow pathways connect these soil-water pools to the artificial drain when enough precipitation initiates subsurface flow. This explanation agrees with our data because flow experiments show macropore flow is solely a mechanism for DRP transport, not a source, and that the surface, or plow layer, is the main contributor to leached P (Djodjic et al., 1999). Kelley et al. (2017) suggest that higher flow years (i.e. spring of 2017) can hydrologically connect previously isolated soil-water stores, increasing dissolved loads. This also agrees with our study as a 15% increase in precipitation with “flashier”, or higher,

discharge rates led to an estimated 70% increase in DRP load at the artificial drain outlet. The cores used in leaching experiments did not have the dissolved P reservoirs because they were harvested late summer, close to, if not at, wilting point, which may explain why we did not see the expected DRP loads even after flushing the cores with enough precipitation as the artificial drain would see in about 3 full years. If this reservoir rich in dissolved nutrients is the main contributor to artificial drain loads, greater soil water stores from increased aggregation due to no-till management (Diaz-Zorita et al., 2004) could increase DRP loads at the artificial drain line outlet in the future. Theoretically, a larger source of DRP that is readily available for plant uptake (Kleinman et al., 2002; Turner et al., 2004) would contribute to increased crop yields, but research suggests that the water that supplies groundwater and streams can move through the subsurface, bypassing the soil-water stores used by plants (Evaristo et al., 2015).

CONCLUSION

Heavy application of fertilizers containing nitrogen and phosphorus for farming use has led to ongoing water quality issues in the United States. When these nutrients leave agronomic systems, and enter water bodies in large quantities, algal bloom and eutrophication can occur. Extensive studies focusing on phosphorus as a pollutant from agronomic systems have been conducted in the many regions of the United States; however, there has been a lack of studies completed in the Palouse region of eastern Washington and western Idaho. This study aimed to determine the P loading potential of a no-till farm system in this dryland cropping region to the local watershed and attempt to determine the conditions and mechanisms that promote subsurface P transport. Soil analyses show a highly variable distribution of P across the sub-catchment area. Initial analysis suggests a significant increase (α= 0.05) in WEP in the subsurface but an overall decrease in combined soil WEP content for all depths from 1999 to 2015. Simulated rainfall experiments show that high-intensity rainfall events can initiate instantaneous flow from soils within the region, providing more evidence of a direct connection from the surface to subsurface drainage systems. However, ponding experiments show that a larger hydraulic conductivity and noticeable preferential flow did not equate to a higher P loading potential. In fact, the soil core with the highest K_s had the lowest WEP, suggesting that some soils have a high retention capacity. The core with the highest K_s also adsorbed the most P from solution, indicating adsorption, can happen rapidly. The artificial drain line that drains the 12-ha subcatchment of the main study site, while being necessary to minimize oversaturated areas that inhibit crop growth, was found to be a considerable source of dissolved reactive P, violating nearby TMDL recommendations during numerous seasonal high flow events over the two-year study timeframe and contributing an estimated average of 0.12 kg P/ha per year to the local watershed. Macropore flow, while being a likely mechanism for subsurface P transport, does not seem to provide an explanation of DRP at the artificial drain outlet. Speciation data from an in-situ drain gauge shows that preferential flow pathways have the capacity to transport non-DRP species but simulated flow experiments on soil cores, speciation data of the artificial drain, and soil-water extracts show a disconnect between P movement through macropore soil and subsurface drainage water which may be explained by the hypothesized soil-water reservoir rich in DRP. Using soil analyses as an attempt to target field areas more susceptible to P loss, we found that WEP correlated strongest with total soil carbon and total soil nitrogen with a good relationship between pH. As CAF continues no-till management and soil carbon and nitrogen are projected to increase, this is likely to lead to an increase in WEP species and thus an increase in the dissolved P load at the artificial drain outlet. This may not be beneficial to crops as our data shows a lack of a relationship between WEP content and crop yield, further suggesting that crops could possibly be drawing water from another source other than the water that supplies Missouri Flat Creek.

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CHAPTER TWO: BROADER IMPLICATIONS AND SUGGESTIONS

INTRODUCTION

Conservation farming practices have become an important focus in today's society where an increasing supply demand due to larger populations must be balanced with maintaining environmental quality. Reducing the impacts of agriculture on our nation's water supplies have prompted enormous amounts of government money into funding conservation efforts. The most recent Farm Bill (2014), for example, offers financial assistance through the Environmental Quality Incentives Program (EQIP) to farmers who enact conservation practices to improve natural resources of all types (NRCS, 2017). Phosphorus (P) management has especially come under extreme scrutiny because even after decades of best management practices (BMPs), water quality issues are still common, most notably around Lake Erie in the Midwestern, USA (Jarvie et al., 2017).

No-tillage or reduced tillage has been shown to be an effective farming strategy in reducing sediment loss (Smith et al., 2015a), increasing crop yields (Diaz-Zorita et al., 2004), and improving overall soil health by increasing organic matter (Tiecher et al., 2012; Zamuner et al., 2008). However, it is starting to become apparent that no-till systems create some environmental concerns that need to be addressed. No-till has been shown to increase soluble P loads in many studies (Gaynor and Findlay, 1995; Sharpley and Smith, 1994; Shipitalo et al., 2013), sometimes as much as doubling the dissolved reactive P concentrations leaving a farm field (Smith et al., 2015a). Normally, P binds tightly to the soil due to its specific chemistry and high affinity to soil particles (Shah et al., 1975; Sims et al., 1998), so it has traditionally been thought that if you reduce overland flow and sediment bound P, you could mostly eliminate P loss, but recent studies have shown that artificial drainage water is a significant source of dissolved and particulate P (King et al., 2014; Smith et al., 2015a, 2015b; Kleinman et al., 2015). Artificial drains are commonly used in areas where excess moisture would create unfavorable growing conditions for crops. Thus, they are necessary to increase crop yields, especially in lowland areas that accumulate water that can be a typical phenomenon with the steep sloping topography of the Palouse region or in wetland areas of the Midwest. However, these artificial drain lines provide a direct route of transfer for agriculturally derived subsurface water to enter nearby water bodies. The proposed mechanism for P loading through no-till fields is an increase in preferential flow through macropores (i.e. soil cracks, earthworm burrows, and decayed root channels). Less disturbance allows the soil to maintain its structure and transport water rich in dissolved nutrients more readily through the subsurface to artificial drainage systems with little contact with the soil matrix where P could be sequestered. The degree of preferential flow can vary widely between systems, but is generally more prevalent in soils with a finer-grained matrix (Beauchemin et al., 1998; Djodjic et al., 2004; Kleinman et al., 2015). The speciation between particulate and dissolved varieties of P in artificial drain water has also been shown to vary greatly between soil types (Eastman et al., 2010; Lam et al, 2016) due to many differing factors relating to adsorption/desorption kinetics (Freese et al, 1995; Grant and Heaney, 1997).

BEST MANAGEMENT PRACTICES OVERVIEW

The Legacy P Dilemma

Phosphorus loads have not seen the expected decreases despite reduced P fertilizer rates and better conservation farming practices and many researchers are attributing this to legacy P in soils (Jarvie et al., 2017; Kleinman et al., 2011; Jarvie et al., 2013). Soils that were once thought to be sinks of P are now proving to be sources as over-application of fertilizer for decades has resulted in P-enriched soils, which contribute more to P runoff (Vadas et al., 2005). The legacy P stores in soils result in a lag time of years, or even decades, between implementing BMPs and a noticeable reduction in P loading (Jarvie et al., 2017) making it difficult to determine if the conservation practices implemented are effective.

Minimal Tillage and Soil Testing

It has been suggested that implementing occasional tillage may be a benefit to some no-till farms as it disrupts preferential flow pathways to prevent event based water from having a direct connection to the artificial drain lines (Williams et al., 2016). Occasional tillage also better incorporates fertilizer into the soil to prevent nutrient stratification and decreases soil aggregation to increase P sorption sites (Kleinman et al., 2011; Williams et al., 2016; Vadas et al., 2008). However, the added benefits may not outweigh the consequences in some systems. Specifically, the Palouse region of eastern Washington and western Idaho, receives the majority of its precipitation in the winter and early spring months when ground cover is minimal. Bare ground from tillage would increase overland flow, especially in frozen soil conditions. Sediment bound P has shown to have concentrations well above that of artificial drain water (See "*Artificial Drainage Water and Stream Dynamics"* in Chapter One) so implementing minimal tillage might exacerbate P loading to the nearby watershed, especially in the face of changing climate patterns (Jarvie et al., 2017), which predict increases in precipitation in the form of rain compared to snowfall (REACCH PNA, 2014). With a history of soil erosion and the steep sloping topography of the Palouse, no-till would be the best overall environmental choice, despite the increased subsurface soluble nutrient loads.

Fertilizer Application Strategies

Immediate fertilizer inputs have been shown to make up the majority of subsurface drainage (Djodjic et al., 1999), so reducing fertilizer rates without negatively affecting crop yields may be the most effective measure in reducing artificial drain P loads. However, with variable soil types resulting in differing available P concentrations, P adsorption behaviors, and hydraulic conductivities, consistent soil testing is the best method for understanding site-specific P dynamics. Soil tests have been shown to directly correlate with dissolved P in runoff (Kleinman et al., 2011), so utilizing them as a method to target relatively enriched-P areas could determine which areas require less fertilizer application.

Fertilizer timing could also have a significant impact on P loading because with a direct connection between the surface and artificial drainage system, a storm event could mobilize fertilizer derived P before it is converted to stable forms or used by the crop. Understanding the precipitation trends of a region is necessary for preventing heavy fertilizer inputs in periods that are more susceptible to runoff.

Surface broadcast of fertilizer has been shown to create nutrient stratification in conservation tillage systems (Sharpley, 2003). Stratification results in nutrient enrichment at the surface but lower depths can be deficient, so it has been proposed that utilizing banded application strategies where fertilizer is directly injected into the soil, typically at rooting depth, is a preferred method for no-till farms (Rehm, 2002). Deep-banding reduces soil contact with P fertilizer to minimize fixation, which occurs when minerals react (Fe- and Al- species at $pH < 5.0$, Ca- species $> pH\ 7.4$) and create immobile phosphates that cannot be directly utilized by crops (Rehm, 2002).

Deep-banding has been shown to be more efficient, decreasing fertilizer quantities, but also requiring more expensive equipment for application (Mahler, 2001).

Vegetated Buffer Strips

One common management strategy is to plant vegetated buffer strips or grassed waterways to intercept water rich in dissolved nutrients (Kelley et al., 2017). Buffer strips are especially useful in areas prone to surface runoff as overland flow rich in particulates would be greatly reduced. This method would be the most beneficial in regions when precipitation correlates with plant growth. In the Palouse the majority of precipitation is received in the winter and early spring, and thus benefits of buffer strip are not as great.

CASE STUDY: THE COOK AGRONOMY FARM

As discussed in chapter one, P loading dynamics of a single field are complex. The Cook Agronomy Farm (CAF) in Pullman, WA, is a prime example of how varying soil types, slopes, and the occurrence of subsurface impeding layers can result in a wide range of soil P and hydraulic conductivities, making it difficult to understand the overall hydrology of a given system. With a wide range of parameters involved, it is hard to suggest strategies for minimizing P loss with only two years of P water quality data. Implementing minimal tillage or vegetated buffer strips may not be successful for the Palouse region because of the climate. Figure 2.1 shows the proposed P budget for the CAF. Minimizing inputs while maximizing crop use and decreasing runoff sources would create a more efficient system overall. Evapotranspiration represents the overwhelming majority of water use (80%), and thus, plant growth is a major sink of available P. Surface runoff and groundwater loss are estimated to make up only 6% of the total water budget (E. Brooks, unpublished data). The most effective management strategy to reduce P loss would be to targeting fertilizer inputs, which vary based on crop and year, and artificial drain outputs (estimated at 14% of the water budget).

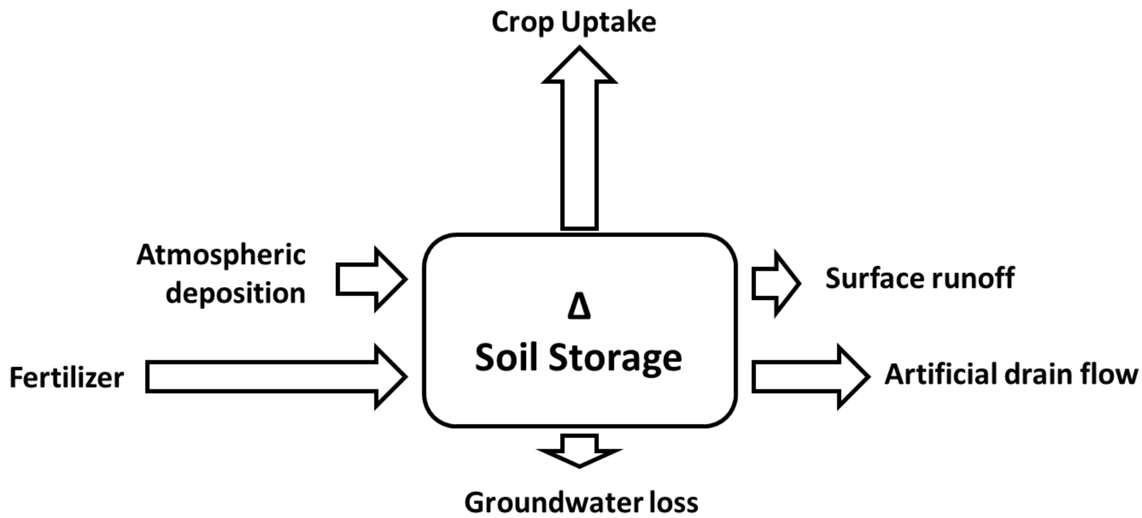

FIGURE 2.1. A visual example of a phosphorus budget for the Cook Agronomy Farm with inputs (atmospheric deposition and fertilizer) and outputs (crop uptake, surface runoff, artificial drain discharge, and groundwater loss).

Given the soil erosion history of the Palouse Region, no-till remains the most beneficial farm management strategy in improving soil health, increasing infiltration, and reducing sediment loss (Tiecher et al, 2012; Gaynor & Findlay, 1995; Smith et al., 2015a), despite the increase in soluble P loads attributed to an increase in hydraulic connectivity to subsurface artificial drains (Jarvie et al., 2017). Consequently, there is a reduction in overland flow at the CAF, reducing surface P loss, which is has DRP concentrations in excess of the surface water TMDL. The artificial drain line at the CAF is required to reduce oversaturation in lowland areas, but transmits an estimated average DRP load of 0.12 kg/ha per year. If the proposed idea of a soil-water pool rich in dissolved P and N exists, we hypothesize best management strategies to increase fertilizer efficiency may help reduce this nutrient pool. Utilizing fertilizer banding compared to broadcast application may be a successful strategy for increasing efficiency and reducing nutrient stratification seen in some no-till systems. Avoiding fertilizer inputs around high precipitation events would be the most beneficial to avoid P loss from preferential flow pathways. Continued soil testing to better understand how specific areas are responding to changing soil P should remain top priority in determining areas requiring more or less fertilizer inputs. We have shown that WEP correlates strongly with total carbon and total nitrogen (Figures 1.23 and 1.24), which can be used to forecast areas more prone to P leaching.

With an estimated P load of 0.09 – 0.15 kg/ $ha^{-1} \cdot yr^{-1}$ (0.20 – 0.33 lbs/ $ha^{-1} \cdot yr^{-1}$) and 2017 diammonium phosphate fertilizer prices estimated at $436 per ton (Silva, 2017), this would equate to a total loss of only $2.44 - $4.14 for the entire 57-ha Cook Agronomy Farm. The minimal potential financial loss may seem of low importance, but P concentrations in drainage water still periodically violate the recommended Total Maximum Daily Load (TMDL) limits, especially with the first flows of the season and in seasonably wet years. However, since the implementation of no-till management in 1998, the CAF has experienced a decrease in WEP content suggesting that overall leaching potential may continue to decrease despite an increasing trend of soil carbon and nitrogen (Unger and Huggins, 2014). Furthering farm research through data collection of soil and water testing will likely result in a more efficient system in the years to come, especially since soil acidification may increase leaching potential from the estimated increase in P availability discussed in the previous chapter.

CONCLUSION

No-till farm management has been shown to be an effective conservation farming practice by reducing soil erosion, increasing crop yields, improving soil health through added organic matter, and increasing infiltration rates. However, tradeoffs are becoming more evident as no-till systems have been found to increase the soluble P loads through preferential flow pathways that provide a direct connection from the surface to artificial drainage systems. Thus, regional factors such as rainfall intensity, subsurface hydrology, and soil types should be taken into account when choosing the best management strategy for a given farm field. Some possible best management strategies have been discussed but effectiveness could be hard to determine due to legacy P soil stores. The Cook Agronomy Farm is an example of a no-till field that has been shown to contribute soluble P loads above local TMDL recommendations but the negative implications of tillage in the Palouse region outweigh the subsurface preferential flow drawbacks attributed to no-till. The possible BMPs discussed may be unfavorable in the climate that is typical of the Palouse where the majority of the precipitation occurs outside the growing season. Understanding seasonal climate is important when determining timing of fertilizer applications and using correlations between WEP and other soil parameters will help forecast areas more susceptible to P leaching. With a lack of long-term water quality data and an overall decrease in WEP content for the soils, it's hard to determine how no-till has affected artificial drain P loads, but the best measure to understand temporal dynamics is through continued data collection of soil and water.

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CHAPTER THREE: FILTER MEMBRANE EFFECTS ON WATER-EXTRACTABLE PHOSPHORUS CONCENTRATIONS FROM SOIL

INTRODUCTION

Total P in water samples is comprised of particulate and dissolved varieties. Dissolved orthophophate, often referred to as dissolved reactive P (DRP), is considered to be the form that directly decreases water quality because it is available for plant uptake. However, particulate or organic forms of P also pose risks for surface water quality degradation because P can be desorbed or solubilized to replenish or increase DRP (Liu et al., 2014; Turner et al., 2002). The potential of particulate P to contribute to the dissolved P load is dependent on its species, with some species more readily available than others to partition into the soluble P phase (Shigaki and Sharpley, 2011). Phosphorus loading and DRP within watersheds is correlated with water-extractable P (WEP) from soils (Kleinman et al., 2002; Pote et al., 1996), and thus WEP is becoming an important laboratory technique to assess the P loading potential of a given soil (Kovar et al., 2009).

To assess water extractable P, filtration of water samples and soil extracts is standard practice. DRP analysis by the molybdate blue colorimetric method is common for water quality monitoring and requires filtration to remove colloids from solution (Pote and Daniel, 2009). For soils, determining water-extractable P (WEP) (Self-Davis et al., 2009), soil-test P (Sims, 2009), and determining P sorption isotherms (Graetz and Nair, 2009) are common laboratory analyses, and all require filtration of soil extracts. Filtration of water and soil solution samples for various analytical methods is necessary because suspended solids can damage equipment and interfere with chemical analysis (Saindon and Whitworth, 2006), and because the dissolved fraction is considered to be the most mobile and bioavailable (Sharpley and Smith, 1993). The dissolved fraction of aqueous solutions is most commonly defined as the portion that passes through a 0.45-µm pore-sized filter membrane (Pote and Daniel, 2009); although some researchers use a 0.2-µm filter (Worsfold et al., 2005). The US Environmental Protection Agency (EPA, 1978) and the United States Geological Survey (Horowitz et al., 1992) provide detailed methods for measuring dissolved constituents in surface water samples, and state that the solutions should be filtered through a 0.45-µm filter (EPA, 1978; Horowitz et al., 1994), which is also the standard pore size for distinguishing between the colloidal and dissolved fractions in soil-water extracts (Kovar et al., 2009).

It has been shown that filter membrane types, even when they have reportedly identical pore-sizes, can play a factor in the analytical determination of dissolved metals in aqueous solutions (Hall et al., 1996; Hedberg et al., 2011; Horowitz et al., 1992; Horowitz et al., 1996). Horowitz et al. (1992) also noted that factors such as sample volumes, whether the sample was pressure applied or vacuum filtered, concentrations of suspended sediment, and grain-size distributions caused changes in Fe and Al concentrations in the filtrate. The osmotic potential for clay particles that act as a semi-permeable membrane has also been reported to cause differences in the filtrate composition (Fritz and Marine, 1983). Saindon and Whitworth (2006) suggested that suspended clay particles in water samples can behave as a semi-permeable membrane during filtration, altering water chemistry and preventing certain dissolved constituents from passing through. This behavior decreases the effective pore size of the filter. However, they found no differences in dissolved P concentrations in Missouri River water samples using different filter types.

There are several different types of filtration equipment, including reusable plate filter assemblies, sealed capsule filters, and syringe or vacuum filtration devices. The U.S. Geological Survey has noted analytical differences in various trace element concentrations (such as Fe, Al, Cr, Co, Cu, etc.) between plate filter assemblies and capsule filters (Horowitz et al., 1994). Capsuled filters are advantageous because they require no pre-cleaning, are sealed devices to minimize contamination, and they are disposable making for ease of use. Thus, the USGS *recommends* that capsule filters be used for most trace elements, but specify either capsule or plate filters can be used in P determination (Horowitz et al., 1994).

While most P analytical methods for water and soils define the pore size of filter membrane to use, membrane material is not typically specified. Filter membrane material has a significant effect on the particle trapping mechanism and efficiency, which may be particularly important for soil runoff or extraction because of the high concentration of suspended solids that include colloids and nano-particles. Most membranes are classified as depth filters, and trap particles on the surface and within the membrane material. A less common membrane type is sieve or screen filters, typically made of polycarbonate, which trap particles only on the surface (Horowitz et al., 1992). Several varieties of membrane materials exist, including polyether sulfone (PES), nylon, and nitrocellulose (NC), which are commonly used membrane material types that are classified as hydrophilic (See product descriptions: https://www.emdmillipore.com/US/en). Many researchers presume that the filter properties are solely defined by whether the material is categorized as hydrophobic or hydrophilic and the listed pore size, and as such, may not take into account different filtration efficiencies that may cause differences in concentrations of P in filtrates.

We hypothesize that filter membrane material is an important determinant in soil extract filtration that affects P concentrations in the filtrate. Thus, the goal of this study was to determine analytical differences in total P concentration (WETP) and DRP concentrations from the WEP test on six soils using three different types of 0.45-µm pore-sized filter membranes. Results will establish if it is necessary to specify membrane material type used in standard soil extraction test methods.

MATERIALS & METHODS

Six soil samples were analyzed using the water-extractable P test (Self-Davis et al., 2009) for total dissolved P (WETP) and dissolved reactive P (DRP) concentrations. Samples K1, 702, and A6 were from three agricultural sites in southern Idaho. Samples 8I, 14L, and 16M were all from a hillslope located on a long-term agricultural study site (Cook Agronomy Farm (CAF)) in the Palouse region of southeastern Washington. The CAF soils were subsurface samples collected from 42 to 123 cm depth. Sample K1 was collected from Kimberley, ID, from 30-60 cm depth. Sample A6 from Aberdeen, ID, and sample 702 from Kimberley, ID, are surface soil samples (0-30 cm). Properties of the soil are listed in Table 1. The samples were collected to be representative of both surface and subsurface soils from various agricultural systems; this study was not designed to make any inferences on available P from the systems.

From each soil, five replicate deionized water extracts were prepared using a 1:10 solid solution ratio following the standard WEP protocol (Self-Davis et al., 2009). In brief, 2 g of soil in 20 mL of 18 MΩ water, shaken for one hour, and centrifuged for 10 minutes at 2,500 rpm. After incubation, each suspension was separated into thirds and each aliquot (about 6.5 mL) was filtered using one of the three different 0.45-µm pore-sized filter membranes: polyether sulfone (PES), nylon, and nitrocellulose (NC) (all membranes are manufactured by of EMD Millipore Inc., Billerica, MA). Reusable, acid-washed, manual pressure syringe-filter assemblies (EMD Millipore Inc., Billerica, MA) were used to hold the membranes for filtration. The suspensions were pushed through the filters using 10 mL polycarbonate syringes. A portion of the filtered extracts were analyzed for WETP measured by inductively coupled plasma atomic emission spectrometer (ICP-AES), and the other split was analyzed for DRP by the Murphy and Riley molybdate blue colorimetric method (Pote and Daniel, 2009). For DRP analysis, some samples only had three or four replicates instead of five. A certified P standard (SPEX Inc., Metuchen, NJ) was diluted to make standards for the calibration curves for the ICP and colorimetric analyses.

Statistical analyses of the data were done using R software version 3.4.0 (R Core Team, 2017). The interaction between soil sample and filter type was found significant (α=0.05) through a two-way analysis of variance (ANOVA). A type-III ANOVA was used for DRP results for the varying sample sizes. Statistical inferences were determined based on a logarithmic transformation of the data and a Tukey's honest significance difference test (α=0.05).

RESULTS

WETP was different for at least one filter type in all six soil sample extracts (α= 0.05) (Figure 3.1). All the soil samples from CAF (14L, 16M, and 8I) had significant differences in WETP between all three membrane types, while the three soil samples from Southern Idaho (K1, 702, and A6) had differences between only two of the membrane types. Differences in WETP for each membrane type between the maximum and minimum values range from 18% (8I) to 35% (K1). The nylon filter membrane had the lowest WETP reading for all six soil samples. In the samples from southern Idaho, the nitrocellulose filter membrane consistently had the highest WETP concentrations, whereas, the highest concentrations in soils from the CAF occurred in extracts filtered through the PES membranes.

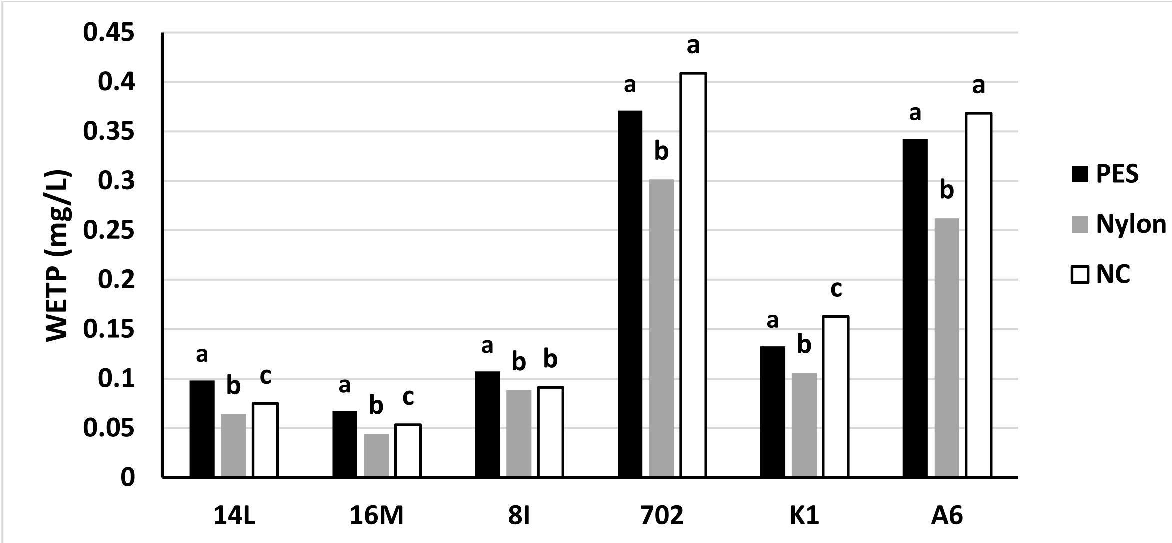

FIGURE 3.1. Total P (WETP) concentrations in water extracts of the six soil samples filtered through three different filter membrane types. Letters indicate significant differences (α = 0.05).

For the southern Idaho soils, differences in DRP values from using different filter membranes ranged from 14% (8I) to 45% (K1) (Figure 3.2), which is similar in magnitude difference to the WETP results for these samples. However, differences in DRP from the CAF soil samples were not as great as the WETP differences. DRP from sample 8I from CAF had no significant differences between membrane types. DRP concentrations from samples 16M and 14L from the CAF filtered through the NC filter membrane were greater than those filtered through the nylon membranes. Amongst the CAF soil samples, the PES membrane filtrate DRP concentration was only different in sample 14L. In the southern Idaho soil samples, the DRP concentrations in the nylon filter were significantly lower than the extracts filtered through the PES and NC membranes, which is similar to results in the WETP analysis; the NC membrane had the highest DRP concentration.

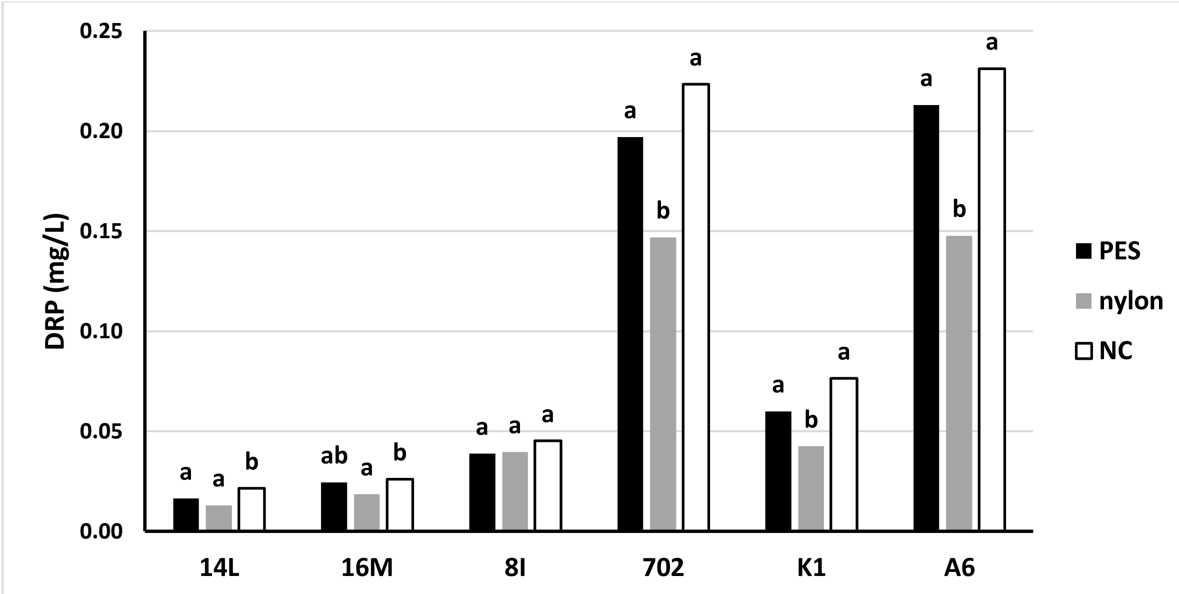

FIGURE 3.2. Dissolved reactive P (DRP) concentrations in water extracts of the six soil samples filtered through three different filter membrane types. Letters indicate significant differences (α = 0.05).

The relationship between WEP and DRP are noticeably different for the two sample regions (Figure 3.3). A clear trend exists in the soils from southern Idaho, whereas, the samples from CAF do not show as clear a trend.

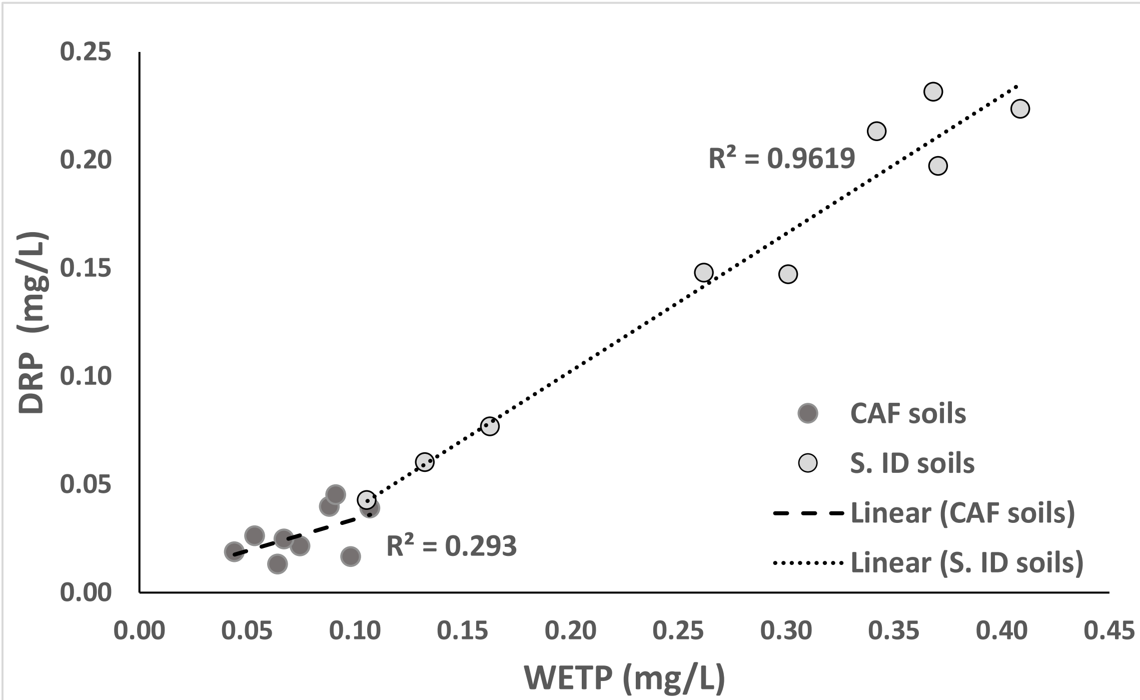

FIGURE 3.3. Relationship between DRP and WETP concentrations for the two soil sample regions using three different filter types.

DISCUSSION

The three membrane types used in this study caused differences in WETP concentrations for all six soil samples. The PES and NC membranes behaved differently between the two soil regions, suggesting that soil characteristics are a major factor during filtration, leading to differences in extractable P concentrations. However, which soil characteristics lead to membrane behavior differences is uncertain. Since clay particles have the ability to cause membrane effects (Fritz and Marine, 1983), soil texture could be an important factor in membrane function. The K1 sample has the greatest percentage of clay- and silt-sized particles (Table 3.1), which may create a colloidal clay-membrane effect, which is affected by membrane type, and thus may explain why this soil had the largest differences in extractable P between the different membrane types. Sample 8I had the lowest percentage of fine grains, and showed the smallest amount of variance in extractable P concentrations. Horowitz et al. (1992) noted that filtration of water with different membrane types yielded varying Fe and Al concentrations. Since P is often associated with Fe and Al in soils and solutions, variances in their concentration may cause differences in filterable P when using different membrane types. In addition to particle size distribution differences, organic carbon may also cause filter membrane performance differences. Organic matter can be particulate or dissolved, and affects particle or colloid aggregation and binds ions, thus changing their solubility. Particulate organic matter may create a membrane-filter effect similar to clay particles, thus changing the membranes effective pore size and efficiency.

TABLE 3.1. Soil properties for the six samples.

	CAF Soils			**Southern Idaho Soils**		
sample	**14L**	**16M**	**8I**	**702**	**K1-3**	**A6-1**
Depth (cm)	42-123	42-123	42-123	0-30	30-60	0-30
pH	6.74	6.90	6.70	7.80	8.02	7.47
%TOC	0.269	0.236	0.220	0.7	0.48	0.65
% Sand	28	38	48	26	10	36
% Silt	58	48	38	57	69	49
% Clay	14	14	14	17	21	15
Textural Class	Silt Loam	Loam	Loam	Silt Loam	Silt Loam	Loam

Filtering the solution through the nylon membrane filter with the syringe was more difficult than it was with the PES and NC membranes. Since the nylon membrane consistently had the lowest WETP and DRP concentrations, it may be more susceptible to clogging and enhanced filtration compared to the PES and the NC membranes. The filtration efficiency decrease may be exacerbated when large amounts of filtrate are needed, or in the case of samples that have a lot of suspended sediment (e.g., colloids and nano-particles).

Based on the consistency between samples for DRP and WETP concentrations, the nylon filter membrane may be the best choice because concentrations were consistently the lowest regardless of the soil. However, the nylon membranes may cause underestimation in soluble P concentrations, which are operationally defined as that which goes through the 0.45-µm filter membrane. In addition, the nylon filter may cause difficulties in filtration because it requires much more pressure to filter the soil extracts through. PES membranes are often touted for their relatively fast filtration speed and have been shown to not retain P during leaching experiments of soil cores (Nelson and Mikkelsen, 2006). However, the observed differences in trends for the PES filters among the two soil regions indicates that membrane performance will vary as a function of soil properties, which could create biases when comparing soluble P form soil extracts between different soils.

CONCLUSION

Results from this study suggest that filter membrane type can lead to significantly different analytical P concentrations in water extracts of soil samples, even though the reported pore size is the same. The use of three different types of 0.45-µm pore-sized filter membranes (polyether sulfone (PES), nylon, and nitrocellulose (NC)) led to statistically significant differences for all six soil samples during the analysis of total water-extractable P (WETP). Differences were also observed in dissolved reactive P (DRP) concentrations, which is a common laboratory test for available dissolved reactive P.

To evaluate soil's P loading potential, laboratory methods need to be precise and accurate. Since extraction of soils with water (WEP) is a common test to evaluate potential loss of P from a soil as runoff, differences in reported concentrations due to method artifacts could lead to discrepancies in monitoring and managing soil P. Based on the results presented in this paper, it is suggested that a standard practice in publishing protocols and analytical methods should be to include filter membrane material to ensure data are consistent and comparable.

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APPENDIX

TABLE 4.1. WEP (mg/kg) results with standard deviations for the nine sample points at the CAF for 1999, 2008, and 2015.

sample name	sample depth	1999 WEP (mg/kg)	sample depth	2008 WEP (mg/kg)	sample depth	2015 WEP (mg/kg)
10D	0-10	7.756 ± 0.047	D-10	9.647 ± 0.013	0-10	6.977 ± 0.140
	31-54	3.910 ± 0.037	20-30	4.469 ± 0.005	20-30	3.452 ± 0.026
	75-133	0.902 ± 0.049	75-133	0.620 ± 0.001	75-133	1.165 ± 0.054
9F	0-10	8.233 ± 0.042	D-10	10.385 ± 0.346	0-10	4.769 ± 0.110
	26-49.5	2.679 ± 0.288	20-30	4.845 ± 0.103	20-30	8.014 ± 0.252
	94-107	0.825 ± 0.064	94-107	10.009 ± 0.035	94-107	1.569 ± 0.076
17F	0-10	7.460 ± 0.180	D-10	8.479 ± 0.172	0-10	7.585 ± 0.128
	18-36	3.354 ± 0.021	20-30	3.558 ± 0.072	20-30	2.877 ± 0.083
	86-114	0.824 ± 0.082	86-114	0.693 ± 0.001	86-114	0.929 ± 0.103
14H	0-10	9.589 ± 0.037	D-10	9.213 ± 0.087	0-10	7.068 ± 0.005
	19-43	4.119 ± 0.049	20-30	4.395 ± 0.039	20-30	4.105 ± 0.111
	89-112	1.449 ± 0.202	89-112	1.912 ± 0.041	89-112	1.415 ± 0.086
16H	0-10	10.490 ± 0.269	D-10	9.504 ± 0.858	0-10	8.426 ± 0.201
	18-36	7.903 ± 0.730	20-30	6.911 ± 0.071	20-30	4.813 ± 0.019
	75-112	1.290 ± -	75-112	1.116 ± 0.066	75-112	1.446 ± 0.038
8I	0-10	3.703 ± 0.107	D-10	8.566 ± 0.872	0-10	5.248 ± 0.049
	23-53	0.915 ± 0.019	20-30	3.133 ± 0.021	20-30	2.835 ± 0.256
	95-120	0.545 ± 0.008	95-120	0.425 ± 0.016	95-120	0.776 ± 0.028
15J	0-10	3.703 ± 0.336	D-10	6.616 ± 0.819	0-10	4.123 ± 0.035
	24-46	1.908 ± 0.074	20-30	2.035 ± 0.042	20-30	2.161 ± 0.098
	77-118	0.637 ± 0.032	77-118	0.367 ± 0.002	77-118	1.253 ± 0.124
14L	0-10	3.183 ± 0.023	D-10	5.031 ± 0.066	0-10	3.811 ± 0.131
	16-42	0.898 ± 0.191	20-30	1.110 ± 0.008	20-30	1.622 ± 0.020
	89-128	1.346 ±0.005	89-128	1.421 ± 0.048	89-128	1.199 ± 0.035
16M	0-10	2.582 ± 0.045	D-10	6.724 ± 0.070	0-10	4.277 ± 0.071
	22-61	1.127 ± 0.002	20-30	1.247 ± 0.000	20-30	1.041 ± 0.080
	96-123	0.337 ± 0.038	96-123	0.283 ± 0.009	96-123	0.482 ± 0.016

TABLE 4.2. Bulk density (g/cm³) from archived data sets and calculated WEP contents (kg P/ha per 10 cm) based on WEP results from Table A1 for the nine sample points at the CAF for 1999, 2008, and 2015.

sample name	sample depth	1999 bulk density (g/cm³)	WEP content (kg P·ha^{-1}·10 cm^{-1})	2008 bulk density (g/cm³)	WEP content (kg P·ha^{-1}·10 cm^{-1})	2015 bulk density (g/cm³)	WEP content (kg P·ha^{-1}·10 cm^{-1})
10D	0-10	1.18	9.19	0.81	7.78	1.09	7.61
	20-30	1.18	4.63	1.18	5.29	1.18	4.08
	75-133	1.58	1.42	1.58	0.98	1.58	1.84
9F	0-10	1.24	10.21	0.91	9.42	0.98	4.69
	20-30	1.24	3.32	1.24	6.01	1.09	8.70
	94-107	1.54	1.27	1.54	1.56	1.54	2.42
17F	0-10	1.19	8.86	0.96	8.12	1.14	8.62
	20-30	1.19	3.98	1.19	4.23	1.28	3.69
	86-114	1.62	1.33	1.62	1.12	1.62	1.50
14H	0-10	1.29	12.32	1.07	9.85	1.17	8.24
	20-30	1.29	5.29	1.29	5.65	1.32	5.41
	89-112	1.46	2.12	1.46	2.79	1.46	2.07
16H	0-10	1.34	14.05	0.91	8.64	1.17	9.87
	20-30	1.34	10.58	1.34	9.25	1.34	6.46
	75-112	1.44	1.86	1.44	1.61	1.44	2.08
8I	0-10	1.43	5.31	0.77	6.64	1.21	6.35
	20-30	1.43	1.31	1.43	4.50	1.45	4.12
	95-120	1.67	0.91	1.67	0.71	1.67	1.30
15J	0-10	1.33	4.92	0.96	6.33	1.21	5.01
	20-30	1.33	2.54	1.33	2.70	1.28	2.76
	77-118	1.26	0.81	1.26	0.46	1.26	1.58
14L	0-10	1.41	4.49	1.04	5.21	1.17	4.45
	20-30	1.42	1.28	1.42	1.58	1.25	2.02
	89-128	1.42	1.92	1.42	2.02	1.42	1.71
16M	0-10	1.24	3.21	0.79	5.34	1.24	5.30
	20-30	1.46	1.64	1.46	1.82	1.48	1.54
	96-123	1.49	0.50	1.49	0.42	1.49	0.72

TABLE 4.3. Speciation results for a subset of the artificial drain and drain gauge samples during the 2016/17 season.

ARTIFICIAL DRAIN					DRAIN GAUGE				
Sample date/time	TP (mg/L)	DRP (mg/L)	non-DRP (mg/L)	% P as DRP	Sample date/time	TP (mg/L)	DRP (mg/L)	non-DRP (mg/L)	% P as DRP
10/30/16 22:33*	0.28	0.212	0.068	75.7	**12/1/16***	<MDL	0.000	-	-
11/28/16 14:14*	0.13	0.109	0.021	83.8	**4/17/2017**	0.030	0.000	0.030	0.00
1/19/17 10:03*	0.14	0.121	0.019	86.7	**4/25/2017**	0.030	0.003	0.026	11.4
1/21/17 12:22*	0.089	0.091	-0.002	102.2⁺	**5/2/2017**	0.020	0.008	0.012	40.4
1/23/17 14:39*	0.099	0.099	0.000	100	**5/10/2017**	0.034	0.000	0.034	0.00
2/5/17 15:54*	0.14	0.109	0.031	77.6	**5/17/2017**	0.049	0.003	0.046	6.88
2/9/17 15:09*	0.13	0.065	0.065	49.7	**5/24/2017**	0.027	0.001	0.026	3.03
2/10/17 20:39*	0.14	0.112	0.028	80.0	**5/30/2017**	0.027	0.003	0.023	12.1
2/18/17 2:47*	0.12	0.079	0.041	66.0	**6/7/2017**	0.049	0.006	0.043	12.6
2/22/17 23:03*	0.085	0.078	0.007	91.3					
2/28/17 13:50*	0.065	0.066	-0.001	101.5⁺					
3/1/17 14:34*	0.073	0.071	0.002	97.3					
3/2/17 16:48*	0.120	0.104	0.016	86.7					
3/3/17 6:02*	0.071	0.068	0.003	95.8					
3/31/17 5:04*	0.063	0.068	-0.005	107.9⁺					
4/2/17 22:39*	0.061	0.067	-0.006	109.8⁺					
4/5/17 12:33*	0.057	0.059	-0.002	103.5⁺					
4/12/17 10:12*	0.065	0.062	0.003	95.4					
4/19/2017 12:22	0.059	0.051	0.008	86.9					
4/27/2017 13:29	0.056	0.052	0.004	92.2					
4/27/2017 13:04	0.020	0.006	0.014	31.4					
5/2/17 12:32*	0.067	0.053	0.014	79.5					
5/3/2017 8:34	0.049	0.041	0.008	83.4					
5/10/2017 8:43	0.056	0.056	0.000	99.3					
5/17/2017 8:53	0.059	0.058	0.001	97.5					
5/30/2017 18:53	0.053	0.047	0.006	87.8					
5/31/2017 12:30	0.059	0.058	0.001	97.5					
6/7/2017 8:57*	0.059	0.044	0.015	73.8					
6/8/2017 4:01	0.059	0.059	0.000	100.0					
6/12/2017 1:30	0.062	0.061	0.001	97.6					
6/19/17 11:55*	0.067	0.055	0.012	82.1					

***Denotes samples analyzed for TP by the Analytical Sciences Lab at the University of Idaho (July 2017)**

⁺ Scaled to 100% for overall average calculations and comparisons with drain gauge samples.

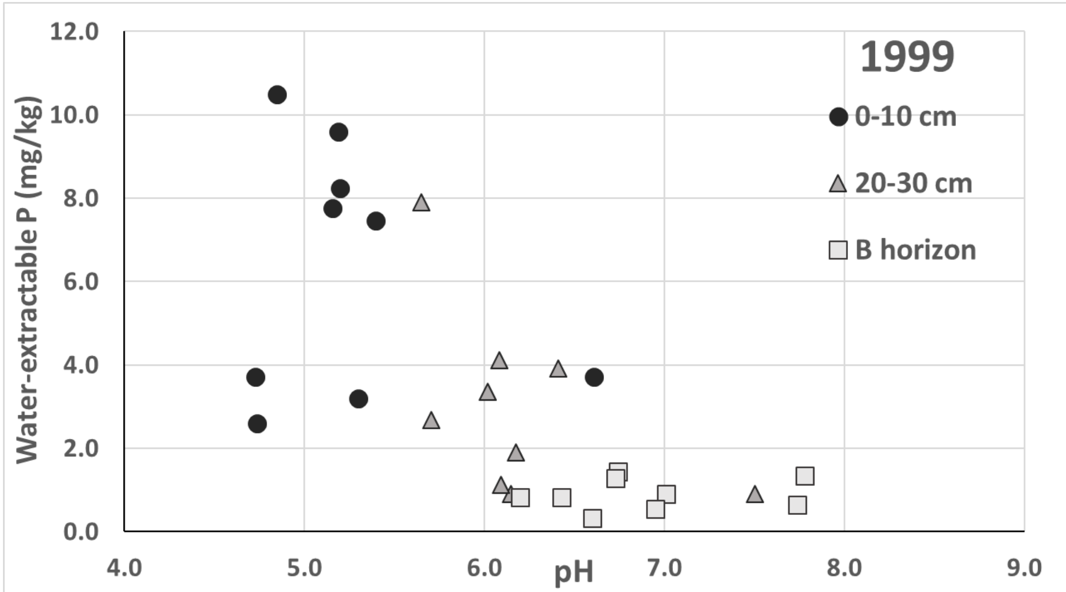

FIGURE 4.1. Water-extractable P (mg/kg) concentrations compared to soil pH for each of the nine sample points separated by depth increment for 1999.

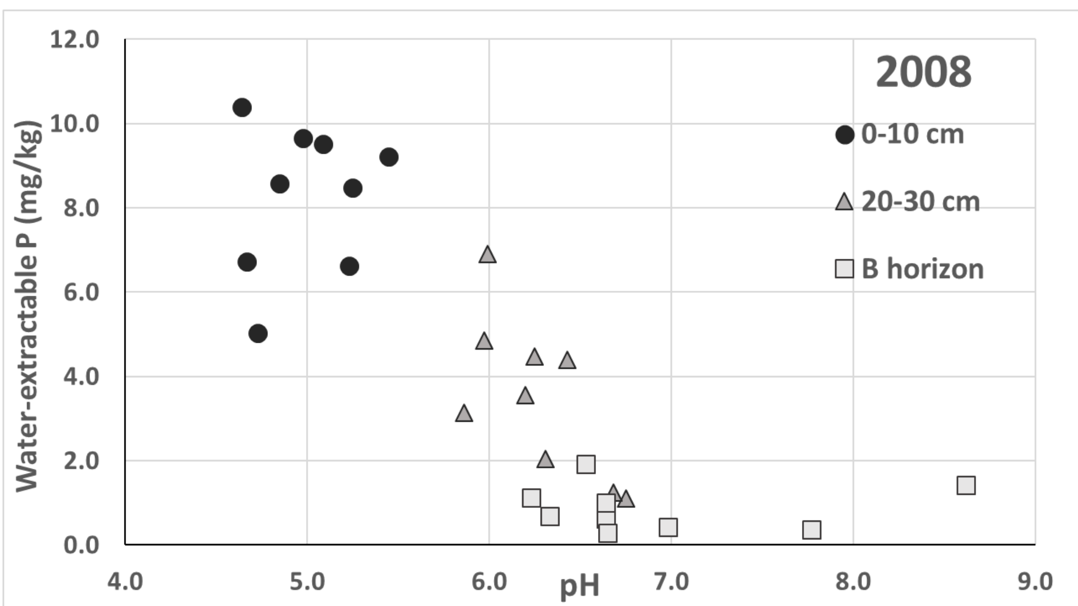

FIGURE 4.2. Water-extractable P (mg/kg) concentrations compared to soil pH for each of the nine sample points separated by depth increment for 2008.

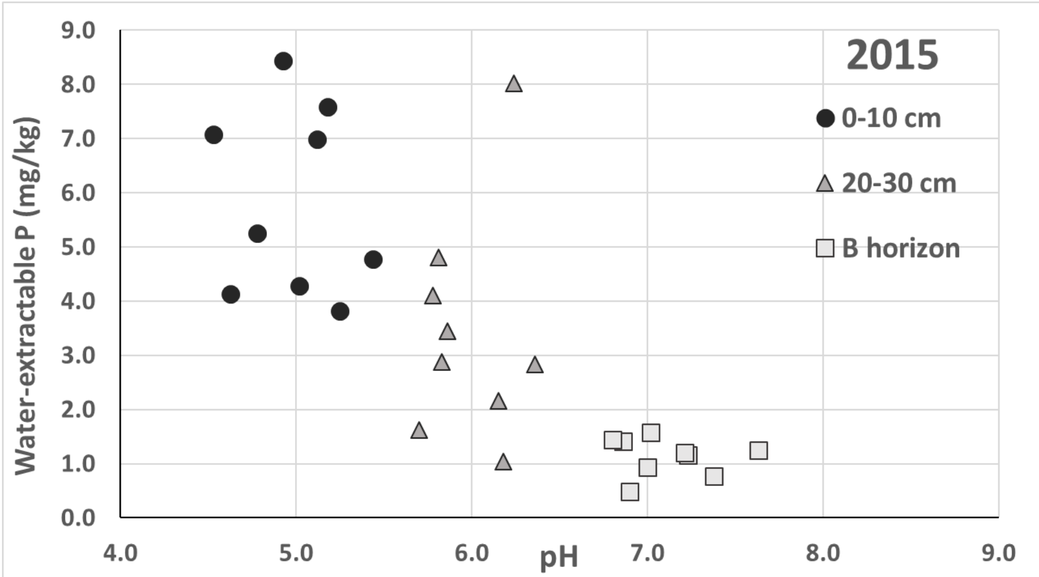

FIGURE 4.3. Water-extractable P (mg/kg) concentrations compared to soil pH for each of the nine sample points separated by depth increment for 2015.

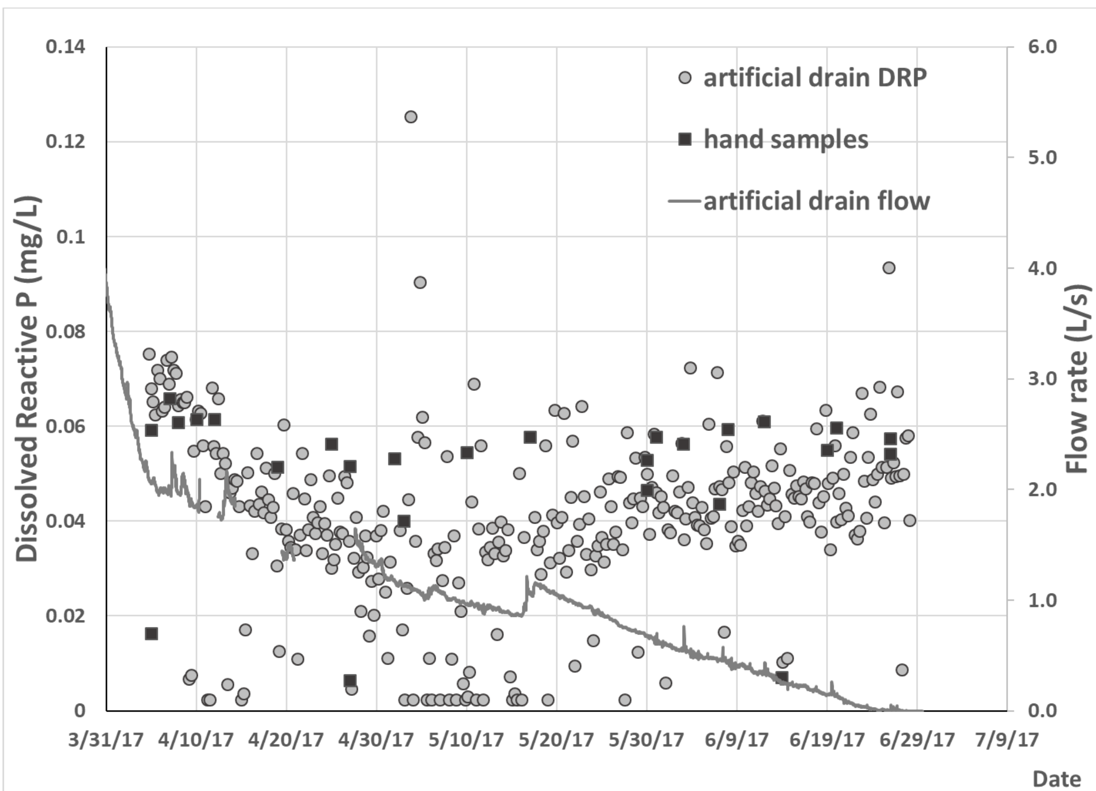

FIGURE 4.4. Phosphate sensor results at the artificial drain outlet for 2016/2017 water year compared with lab analyzed hand samples taken during the same time-frame.

LOADEST CALIBRATION DETAILS

Calibration (Load Regression)

Number of Observations : 224

Number of Uncensored Observations: 224

"center" of Decimal Time : 2016.661

"center" of Ln(Q) : -4.5943

Period of record : 2015-2017

<u>Model Evaluation Criteria Based on AMLE Results</u>

Model #	AIC	SPPC
1	2.238	-254.048
2	2.246	-256.672
3	2.157	-246.732
4	2.105	-242.608
5	2.148	-247.345
6	2.110	-244.865
7	2.099	-243.572
8	2.093	-244.704
9	2.102	-247.334

Akaike Information Criterion (AIC) and Schwarz Posterior Probability

Criteria (SPPC) did not select same best fit model. Model # 8

selected on basis of AIC. (Model # 4 would have been selected based on SPPC)

Selected Model:

Ln(Load) = a0 + a1 LnQ + a2 LnQ^2 + a3 Sin(2 pi dtime) + a4 Cos(2 pi dtime) + a5 dtime

where:

Load = constituent load [kg/d]

LnQ = Ln(Q) - center of Ln(Q)

dtime = decimal time - center of decimal time

Model Coefficients

	a0	a1	a2	a3	a4	a5
AMLE	-6.3791	1.1201	0.0238	0.3558	0.3703	-0.2496
MLE	-6.3791	1.1201	0.0238	0.3558	0.3703	-0.2496
LAD	-6.2576	1.0467	0.0105	0.2780	0.1496	-0.1095

AMLE Regression Statistics

R-Squared [%] : 84.00

Residual Variance : 0.4625

Serial Correlation of Residuals: 0.0302

Prob. Plot Corr. Coeff. (PPCC) : 0.7426

Significance Level of PPCC Test: 3.123E-20

Coeff.	Std.Dev.	t-ratio	P Value
a0	0.1063	-60.01	1.702-141
a1	0.0454	24.66	7.263E-67
a2	0.0135	1.76	7.490E-02
a3	0.0906	3.93	9.051E-05
a4	0.1806	2.05	3.859E-02
a5	0.1047	-2.38	1.640E-02

Correlation Between Explanatory Variables

Explanatory variable corresponding to:

	a1	a2	a3	a4
a2	0.0000			
a3	-0.0741	-0.0011		
a4	-0.6877	-0.1682	-0.1856	
a5	0.1964	0.3196	-0.5192	-0.0792

Additional Regression Statistics:

MLE Residual Variance: 0.4625

Comparison of Observed and Estimated Loads

The summary statistics and bias diagnostics presented below are based on a comparison of observed and estimated loads for all dates/times within the calibration data set. Although this comparison does not directly address errors in load estimation for unsampled dates/times, large discrepancies between observed and estimated loads are indicative of a poor model fit. Additional details and warnings are provided below.

Note: The comparison that follows uses a concentration equal to 1/2 the detection limit when an observation is censored. The summary stats and bias diagnostics are therefore slightly inaccurate for censored data sets.

Bias Diagnostics

Bp [%]	13.559
PLR	1.136
E	0.797

Bp : Load Bias in Percent

Positive (negative) values indicate over (under) estimation.

The model should not be used when the + or - bias exceeds 25%

PLR Partial Load Ratio

Sum of estimated loads divided by sum of observed loads.

Values > 1 indicate overestimation; values < 1 indicate underestimation.

PLR = (Bp + 100) / 100

E Nash Sutcliffe Efficiency Index

E ranges from -infinity to 1.0

E = 1; a perfect fit to observed data.

E = 0; model estimates are as accurate as the mean of observed data.

E < 0; the observed mean is a better estimate than the model estimate